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CLV.—THE POLYIODIDES OF POTASSIUM, RUBIDIUM AND CAESIUM.

BY H. W. FOOTE AND W. C. CHALKER.

The polyiodides of the alkalis have recently been investigated by Abegg and Hamburger,[1] who have attempted to determine all those that form stable solids at 25°. The method used by these investigators consisted essentially in treating an alkali iodide with varying amounts of benzene which was nearly saturated with iodine and shaking the mixtures in a thermostat till there was no further change in the concentration of iodine in the benzene. By this process iodine was withdrawn from solution by the alkali iodide, which was partially converted into a periodide. The concentration of iodine in the benzene solution when equilibrium was reached was constant as long as the two iodides were present as solids. The concentration changed to a new and constant value when the amount of iodine present was sufficient to convert all the iodide into a mixture of periodides. By taking into account the amount of the constituents used and noting when the changes in concentration occurred, the authors drew conclu-

[1] Z. anorg. Chem., 50, 403, 1906.

sions in regard to the composition of the polyiodides which were formed. They concluded that the following periodides exist as solids at 25°:

KI_7; NH_4I_3; RbI_3, RbI_7, RbI_9; CsI_3, CsI_5 or CsI_7, CsI_9.

The method which was used is undoubtedly correct in principle and might lead to correct conclusions, but the compounds differ widely from those obtained before by other investigators.

Johnson[1] has described the compound KI_3, which was not found by Abegg and Hamburger. He analyzed it repeatedly and determined its specific gravity. The same compound has also been obtained by Wells and Wheeler[2] and its crystallography determined. The periodides of rubidium and caesium have been investigated by Wells and by Wells and Wheeler,[3] who obtained the compounds RbI_3, CsI_3 and CsI_5. These authors state that attempts to prepare an iodide higher than KI_3 or RbI_3 were unsuccessful. The solubility relations of the periodides of caesium have been studied by Foote,[4] but this work seems to have been overlooked by Abegg and Hamburger. The solubility in water of varying mixtures of caesium iodide and iodine was determined at temperatures both above and below 25°, the temperature at which Abegg and Hamburger worked. The method was in principle not unlike that used later by Abegg and Hamburger but it had the advantage that both caesium iodide and iodine dissolved in water and could be determined, while in benzene only iodine was determined. Just as in the benzene solution, constant concentration of iodine indicated a mixture of two iodides, so here a constant concentration of caesium iodide and iodine indicated a mixture. When the composition of the solution changed to a new constant value it indicated a change in the solid phases present, precisely as was the case with the benzene solution. Knowing the amounts of the constituents present, it was an easy matter to determine what solid phases were

[1] J. Chem. Soc., **1877**, 249.
[2] Z. anorg. Chem., **1**, 442.
[3] *Ibid.*, **1**, 85, 442; **2**, 255.
[4] THIS JOURNAL, **29**, 203 (1903).

present. The following table, taken from the article referred to, gives the results obtained:

Table I.—Solubility of Caesium Iodides.

Temperature.	(1) Pure CsI. CsI. Per cent.	(2) CsI and CsI_3. CsI. Per c't.	I. Per c't.	(3) CsI_3 and CsI_5. CsI. Per c't.	I. Per c't.	(4) CsI_5 and I. CsI. Per c't.	I. Per c't.
Cryohydric	27.73	27.53	0.09	3.14	0.25	0.88	0.35
	27.64	27.51	0.09	3.59	0.35	0.84	0.34
T =	—4°.0	T=—	4°.0	2.82	0.35	0.83	0.34
				T=—	0°.4	T=—	0°.2
35°.6	51.35	51.49	0.71	10.67	1.75	3.66	1.47
	51.61	51.84	0.71	10.78	1.86	3.82	1.73
52°.2	...	...	....	16.51	4.34	6.45	3.52
				17.06	4.70	6.99	3.13
						6.87	3.29
						6.44	3.61

In the table, it will be noticed that the composition of the solutions under (2), (3) and (4) was constant at a given temperature, although the residues which gave constant results were purposely varied greatly. From the results it was concluded that CsI_3 and CsI_5 are formed at all the temperatures investigated and that no other periodides are formed.

The objection that may be raised to the results given in the table is that the composition of the residues is not given—an objection that holds to a great extent in the results of Abegg and Hamburger—so that, for instance, the results under (4) would not show that CsI_9 did not exist since it was not shown that the residues in the experiments contained percentages of iodine both greater and less than the percentage of iodine in CsI_9. While the composition of the residues was varied greatly, we do not now know their exact composition and it seemed advisable to carry out a few experiments at 25° by the same method used before and, in addition, to determine accurately the composition of the residues. We have also carried out similar experiments with potassium and rubidium iodides.

In every case weighed amounts of the iodide and iodine were treated with a known quantity of water in small glass-stoppered bottles. The heads of the bottles were dipped in

melted paraffine to make them perfectly tight. The bottles were usually warmed for some time in a beaker of water, with thorough shaking, and then placed in a thermostat kept at 25° and shaken for a number of days. We had no difficulty, under these conditions, in obtaining saturated solutions. The liquid was removed for analysis by drawing it into a pipette through a plug of glass wool. The liquid was weighed in two portions. One portion was used to determine available iodine by titration with thiosulphate. Alkali iodide was determined in the other by evaporating to dryness and igniting gently. The residues were freed from the mother liquors as rapidly and thoroughly as possible by pressing between filter paper. Alkali iodide was determined in them by ignition.

Caesium Polyiodides.

Most of the caesium iodide-iodine mixtures were prepared by using calculated amounts of caesium triiodide in place of caesium iodide, as we had a supply of exceedingly pure triiodide on hand. One or two mixtures, however, were prepared by using caesium iodide obtained by igniting the triiodide. It was an easy matter to prepare mixtures in which the residues, after shaking, would have approximately any composition desired, since the composition of the solutions at 25° could be approximately calculated in advance by interpolation from the results in Table I.

As there appears to be no question that CsI_3 forms and that no periodide lower than this exists, only those mixtures were prepared whose residues would contain more than 49.42 per cent available iodine, which is the amount in caesium triiodide. The following results were obtained:

Table II.—Solubility of Caesium Iodides at 25°.

	Solution.		Residue.	Empirical composition of residue.	Residue contains:
	Per cent CsI.	Per cent I.	Per cent available I.		
1	7.72	1.18	52.86	$CsI_{3.29}$	CsI_3 and
2	7.69	1.19	59.32	$CsI_{3.98}$	CsI_5
3	2.40	1.23	69.88	$CsI_{5.75}$	CsI_5
4	2.35	1.23	75.84	$CsI_{7.43}$	and
5	2.39	1.25	89.93	$CsI_{19.3}$	Iodine

The results are very sharp and confirm the results obtained by Wells and Wheeler and our own previous conclusions that only CsI_3 and CsI_5 exist as solids at 25°. They show constant solubility while the composition of the residue lies between that of CsI_3 and CsI_5 and they show a second constant solubility for all mixtures higher in iodine than corresponds to CsI_5, proving that CsI_7 and CsI_9 do not form. If CsI_9, for instance, had formed, the solubility in No. 4 would have been different from that in No. 5, since different phases would have been present.

Potassium Polyiodides.

The periodides of potassium are extraordinarily soluble in water, but when this was taken into account it was not a difficult matter to prepare mixtures which gave residues, after shaking, varying from nearly pure potassium iodide to nearly pure iodine. The results obtained when mixtures of two iodides were present in the residues are given in Table III.

Table III.—Solubility of Potassium Iodides at 25°.

	Solution.					
	(1)	(2)	(3)	Residue.		
	Per cent KI.	Per cent I.	Per cent I minus per cent KI.	Per cent KI.	Empirical composition.	Residue contains:
1	29.45	64.34	34.89	94.10	$KI_{18.2}$	KI and
2	28.91	63.88	34.97	44.28	$KI_{2.65}$	KI_3
3	26.84	66.54	39.70	29.81	$KI_{4.08}$	KI_3
4	27.18	67.14	39.96	27.73	$KI_{4.41}$	and
5	27.14	66.60	39.46	19.29	$KI_{6.48}$	KI_7
6	25.88	68.79	42.91	16.16	$KI_{7.79}$	KI_7 and
7	25.57	69.01	43.44	11.96	$KI_{10.6}$	Iodine

The change in concentration from one constant value to the next, when the solid phases change, is slight. It can perhaps be shown best by the difference between the concentration of iodine and potassium iodide, which is given in column (3). It will be seen that the solubility remains constant in each group. It changes when the residues change from the empirical composition $KI_{2.65}$ to $KI_{4.08}$, showing that

KI_3 undoubtedly exists. This confirms the work of Johnson and of Wells and Wheeler but does not agree with the results obtained by Abegg and Hamburger. The solubility changes again when the residue changes from $KI_{6.48}$ to $KI_{7.79}$, showing the formation of KI_7. This is the only one of the five new compounds described by Abegg and Hamburger whose existence we have been able to confirm.

Mixtures were also prepared in which the constituents were present in such proportions that the pure compounds would be formed. It is evident that pure potassium triiodide can exist in contact with solutions varying from the composition of Nos. 1 and 2 to that of Nos. 3 to 5 (Table III.), and the heptaiodide with solutions varying from the composition of Nos. 3 to 5 to that of Nos. 6 and 7. The following results (Table IV.) give the composition of solutions and residues when the pure compounds were present:

Table IV.—Solubility of Potassium Iodides at 25° (Continued).

	Solution.		Residue.	
	Per cent KI.	Per cent I.	Per cent KI.	Residue contains:
1	27.86	66.56	40.54	KI_3
2	27.27	66.91	40.11	Calculated per cent KI = 39.55
3	26.95	67.17	18.52	KI_7
4	25.71	67.91	18.60	Calculated per cent KI = 17.96

We consider the results in Tables III. and IV. sufficient to show that the compounds KI_3 and KI_7 are the only periodides which form solids at 25°.

Rubidium Periodides.

To prepare rubidium iodide, we used rubidium chloride which had previously been very carefully purified in this laboratory. It was converted into the nitrate and then into the carbonate by strong ignition with an excess of pure oxalic acid. This was dissolved in hydriodic acid and evaporated to dryness.

The entire series of results obtained is given below (Table V.):

Table V.—Solubility of Rubidium Iodides at 25°.

	Solution.		Residue.	Empirical	Residue
	Per cent RbI.	Per cent I.	Per cent RbI.	composition.	contains:
0	61.93	0	100	RbI	RbI
1	59.99	5.87	93.75	$RbI_{1.11}$	RbI
2	59.88	5.93	58.34	$RbI_{2.20}$	RbI_3
3	57.24	8.02	46.33	$RbI_{2.94}$	RbI_3
4	33.89	38.08	45.42	$RbI_{3.01}$	
5	28.01	64.85	37.95	$RbI_{2.74}$	RbI_3
6	27.85	65.12	29.70	$RbI_{4.98}$	and
7	27.83	65.13	23.57	$RbI_{5.43}$	
8	27.99	64.98	14.09	$RbI_{11.2}$	Iodine

From the results it will be seen that the solubility is constant in Nos. 1 and 2, where a mixture of RbI and RbI_3 is present, and it is constant again in Nos. 5 to 8, where the residues vary from the empirical composition $RbI_{3.74}$ to $RbI_{11.2}$. The latter results show that RbI_7 and RbI_9 did not form, which agrees with the observations of Wells and Wheeler.

Summary.

1. Abegg and Hamburger state that the following alkali periodides form at 25°: KI_7, RbI_3, RbI_7, RbI_9, CsI_3, CsI_5 or CsI_7, CsI_9.

2. Previous investigators have found the following compounds: KI_3, RbI_3, CsI_3, CsI_5.

3. We have found at 25° the compounds KI_3, RbI_3, CsI_3, CsI_5 described by previous investigators, and also KI_7, described by Abegg and Hamburger. We find no indication whatever of the existence of the compounds RbI_7, RbI_9, CsI_7 and CsI_9, mentioned by Abegg and Hamburger.

[Contributions from the Chemical Laboratory of Harvard College.]

MERCURY SALTS OF THE THREE NITRANILINES.

BY C. LORING JACKSON AND R. W. PEAKES.

The abnormal replacement of bromine by hydrogen in 1,3,5-tribrom-2,4-dinitrobenzene and allied compounds has been

studied for some years in this laboratory. In the hope of finding new cases of this sort, we undertook the investigation of the behavior of this substance with the 3 nitranilines, and when, as was not entirely unexpected, the two substances did not react under any conditions we could find, we prepared the mercury salts, which might well give a better result.

On boiling a nitraniline with water and freshly prepared mercuric oxide, a red salt was formed, which, however, under these conditions, we could not obtain free from mercuric oxide, even when a large excess of the nitraniline was used; but, when the mercuric oxide acted in the nascent state, the substances were obtained pure with little trouble. The process consisted in mixing aqueous solutions of the nitraniline and mercuric nitrate and adding to the mixture potassic hydrate, when, after standing, the salt came down as a red precipitate, which was purified by washing with water and ether.

The para and ortho salts have the formula $(C_6H_4NO_2NH)_2Hg$; the meta salt seems to be $(C_6H_4NO_2NH)_2Hg.H_2O$. This theory derived from the analyses is supported by the fact that it has a much deeper color than the other two salts, being maroon while the para salt is vivid crimson and the ortho bright red. If this darker color is due to a molecule of water of crystallization, it is probable that the para salt also was occasionally deposited with water of crystallization, since now and then it appeared of a purplish-crimson color, which turned to bright crimson, with no trace of purple, on drying *in vacuo*. Of the three salts, the ortho was formed most rapidly, the meta next, and the para most slowly. The salts proved much less reactive than had been hoped, as they gave no better results with the tribromdinitrobenzene than the free nitranilines, although, on the other hand, they were decomposed by iodine in benzene solution, and hydrochloric acid dissolved them at once.

So far as we can find, these salts are new, but Pesci,[1] by the same process, had obtained the aniline salt, $(C_6H_5NH)_2Hg$, some years previously. Although our salts undoubtedly

[1] Gazz. chim. ital., **28** [2], 443.

correspond to Pesci's, there are marked differences between the two sets in physical properties, since the aniline salt is colorless and somewhat soluble in water, while the nitraniline salts are intensely colored in various shades of red and essentially insoluble.

EXPERIMENTAL.

Preparation of the Mercury Salts of the Three Nitranilines.—A saturated solution of the nitraniline in water at ordinary temperatures was made, and to one liter of this was added slowly, with constant stirring, an aqueous solution of mercuric nitrate containing enough nitric acid to hold the salt in solution. The reagents were mixed in the proportion of a little more than one molecule of the nitrate to two of the nitraniline, the amount of the latter being calculated from its solubility in water, which gave a sufficiently accurate result for this purpose. A strong solution of potassic hydrate was then added slowly and with constant stirring until the alkali was present in excess, when the mixture was allowed to stand for some time with occasional stirring. On the addition of the potassic hydrate there was at first a slight milky precipitation, which was soon replaced by the dark-red mercury salt. With ortho- or metanitraniline the standing, after the addition of the alkali, should last over an hour; with the para compound, much longer. In working with the metanitraniline we were sometimes embarrassed by the formation of a brown, inorganic precipitate, which we recognized as the oxychloride of mercury, formed from an impurity of chloride in the potassic hydrate used. Its formation was usually avoided by adding the alkali more rapidly than in the case of the para or ortho body. After the precipitate of the organic salt had formed and settled, the supernatant liquid was decanted and the solid washed on a filter several times with water, which removed the inorganic impurities and part, but not all, of the nitraniline. The precipitate was then dried and washed with ether until the washings became colorless, when it was dried *in vacuo* for analysis.

The same salts, to judge from their color, were formed on boiling the nitranilines with freshly precipitated mercuric

oxide and water, but we did not succeed in converting all the mercuric oxide into the salt, even when a large excess of nitraniline was used, and therefore abandoned this method of preparation. Mercuric nitrate gave no precipitate with a cold solution of a nitraniline but formed one, to a limited extent, with a hot, saturated solution; as this precipitate seemed to be a mixture of several substances, we did not undertake its study.

Paranitraniline Salt, $(C_6H_4NO_2NH)_2Hg$.—All the salts were analyzed by dissolving in water and hydrochloric acid and precipitating with sulphuretted hydrogen the mercuric sulphide, which was weighed on a Gooch crucible. Washing the mercuric sulphide with carbonic disulphide, in one or two cases, produced no change in weight.

I. 0.3588 gram substance gave 0.1727 gram HgS.
II. 0.6622 gram substance gave 0.3175 gram HgS.
III. 0.1346 gram substance gave 0.0647 gram HgS.

	Calculated for $(C_6H_4NO_2NH)_2Hg$.	Found. (I.)	(II.)	(III.)
Hg	42.19	41.50	41.33	41.45

Properties of the Paranitraniline Salt.—This salt is precipitated sometimes as a purplish-crimson powder, which becomes brilliant crimson on drying; in other preparations the precipitate is brilliant crimson from the first. It seems to be slightly soluble in pyridine but insoluble in water, alcohol, ether, acetone, chloroform, ethyl acetate or benzene. It is slowly decomposed by standing with alcohol. Hydrochloric acid decomposes and dissolves it.

Metanitraniline Salt, $(C_6H_4NO_2NH)_2Hg.H_2O$.

I. 0.1188 gram substance gave 0.0559 gram HgS.
II. 0.4584 gram substance gave 0.2128 gram HgS.
III. 0.4743 gram substance gave 0.2205 gram HgS.

	Calculated for $(C_6H_4NO_2NH)_2Hg$.	Found. (I.)	(II.)	(III.)
Hg	42.19	40.57	40.00	40.08

These analyses show that the substance is not the simple salt, as was the case with the paranitraniline. If it contains

one molecule of water of crystallization, the percentage of mercury is as follows:

	$(C_6H_4NO_2NH)_2Hg.H_2O.$
Hg	40.64

This value agrees sufficiently well with those found. The theory that the meta compound contains water of crystallization receives a certain confirmation from the fact that it has a much darker color than either the para or the ortho salt, and it can be accepted with safety, we think, until it has been tested by experiment.

Properties of the Metanitraniline Salt.—It forms a maroon-colored powder when dried *in vacuo*. The precipitate is less bulky and forms more slowly than that from the orthonitraniline, but forms more quickly and is more bulky than the para salt. It is insoluble in water or the common organic solvents.

Orthonitraniline Salt, $(C_6H_4NO_2NH)_2Hg$.

I. 1.2282 grams substance gave 0.6001 gram HgS.
II. 0.5346 gram substance gave 0.2550 gram HgS.
III. 0.4786 gram substance gave 0.2288 gram HgS.

	Calculated for $(C_6H_4NO_2NH)_2Hg$.	Found. (I.)	(II.)	(III.)
Hg	42.19	42.12	41.11	41.20

The necessity for washing with ether was shown by the analysis of a specimen washed only with water, which gave 40.89 per cent of mercury.

Properties of the Orthonitraniline Salt.—A bright-red powder, which forms more quickly and appears as a more bulky precipitate than the two isomeric salts. Insoluble in water and the common organic solvents.

After we had determined that 1,3,5-tribrom-2,4-dinitrobenzene did not react on the nitranilines either in solution in water, alcohol, or alcohol and benzene, or when the two substances were fused together, we tried the action of the same tribromdinitrobenzene on our mercury salts, both in presence of benzene and of benzene and alcohol, but even after 9 hours' boiling there were no signs of a reaction. Iodine, on the other hand, in benzene solution, acted upon the mercury salts,

but the work was undertaken too late in the year for us to study the product.

Attempts to Make Other Nitraniline Salts.—Solutions of orthonitraniline in water were added, in one experiment, to a solution of cupric sulphate, in another to a solution of plumbic acetate; on adding potassic hydrate the metallic hydrate was obtained in each case with no admixture of an organic salt.

In the hope that the hydrogen attached to the nitrogen might be replaced by sodium if it were rendered more reactive, the benzoylnitranilide was made by allowing the solid nitraniline to stand with benzoyl chloride overnight (so far as we can find it has not been made in this way before); and this compound, dissolved in absolute alcohol, was allowed to stand with sodic ethylate, but, although the solution turned yellow, on addition of ether no precipitate was obtained. It seems probable, therefore, that no salt was formed, which is strange when it is remembered that acetanilide gives a sodium salt.

CAMBRIDGE, MASS.,
August 29, 1907.

DIETHYLISOPROPYLMETHANE.

BY LATHAM CLARKE.

This paper describes the synthesis of diethylisopropylmethane, which forms part of a research on the octanes, undertaken some time ago in this laboratory.[1]

The hydrocarbon was made by two different methods, and in this way its constitution was confirmed.

In the preparation of diethylisopropylmethane, the simplest procedure is as follows: From ethyl acetacetate is made ethyl diethylacetacetate which, on saponification, gives 3-ethyl-2-pentanone or diethylacetone, $CH_3COCH(C_2H_5)_2$. This is subjected to the Grignard reaction, using magnesium and methyl iodide, and a carbinol is produced, having the structure

$$(CH_3)_2C(OH)CH(C_2H_5)_2,$$

[1] Preliminary notice, Ber. d. chem. Ges., 40, 352.

which, when converted into the corresponding carbinol iodide and reduced, yields the desired octane.

To summarize these reactions:

$$CH_3COCH_2CO_2C_2H_5 \rightarrow CH_3COC(C_2H_5)_2CO_2C_2H_5 \rightarrow$$
$$CH_3COCH(C_2H_5)_2 \rightarrow (CH_3)_2C(OH)CH(C_2H_5)_2 \rightarrow$$
$$(CH_3)_2C(I)CH(C_2H_5)_2 \rightarrow (CH_3)_2CHCH(C_2H_5)_2.$$

The second method consists in making ethyl ethylisopropylacetacetate and saponifying it, with the formation of 3-isopropyl-2-pentanone, or ethylisopropylacetone,

$$CH_3COCH(C_2H_5)(CH(CH_3)_2).$$

By reducing this to the carbinol, converting the carbinol into the corresponding carbinol iodide, and reducing, the octane diethylisopropylmethane is obtained. These reactions may be summarized as follows:

$$CH_3COCH_2CO_2C_2H_5 \rightarrow CH_3COC(C_2H_5)(CH(CH_3)_2)CO_2C_2H_5 \rightarrow$$
$$CH_3COCH(C_2H_5)(CH(CH_3)_2) \rightarrow$$
$$CH_3CHOHCH(C_2H_5)(CH(CH_3)_2) \rightarrow$$
$$CH_3CH(I)CH(C_2H_5)(CH(CH_3)_2) \rightarrow$$
$$CH_3CH_2CH(C_2H_5)(CH(CH_3)_2).$$

Both methods yielded identical products.

The first method is, however, the better one, as the reactions proceed more smoothly and the yield is better. In the second method, in the saponification of ethyl ethylisopropylacetacetate by caustic potash, the reaction takes place very slowly, the yield of the ketone, 3-isopropyl-2-pentanone,

$$CH_3COCH(C_2H_5)(CH(CH_3)_2),$$

being only about 25 to 30 per cent of the theoretical after a week's treatment. The great stability toward alkalis manifested by the ester,

$$CH_3COC(C_2H_5)(CH(CH_3)_2)CO_2C_2H_5,$$

is accounted for by the spatial configuration. The ethyl and the large isopropyl group, both of which are on the same carbon atom, shield the carboxyl from the splitting

action of the alkali. It is interesting to note that the corresponding diethyl derivative of ethyl acetacetate,

$$CH_3COC(C_2H_5)_2CO_2C_2H_5,$$

is decomposed almost completely under the same conditions by 8 hours' boiling.

EXPERIMENTAL.

First Method.

Ethyl diethylacetacetate, $CH_3COC(C_2H_5)_2CO_2C_2H_5$, was prepared by Conrad's method,[1] and saponified by boiling for 8 hours with a 10 per cent solution of caustic potash. The resulting ketone was distilled with steam, separated, dried with calcium chloride, and fractionated several times with great care with a Hempel column until a fraction boiling sharply at 138° at 760 mm. pressure was obtained. Ethyl diethylacetacetate usually gave a yield of 60 per cent of 3-ethyl-2-pentanone of this degree of purity.

3-Ethyl-2-methyl-2-pentanol, $(CH_3)_2C(OH)CH(C_2H_5)_2$. — 3-Ethyl-2-pentanone, a ketone containing seven carbon atoms, was converted into 3-ethyl-2-methyl-2-pentanol, a carbinol with eight carbon atoms, by the Grignard reaction.

Twenty-four grams of magnesium turnings were dissolved in a mixture of 160 grams of methyl iodide and 100 grams of dry ether. To this, the ketone (100 grams), which was mixed with an equal volume of ether, was slowly added and the mixture set aside overnight. Next day ice and water were added until the magnesium-organic body was decomposed, and the mixture was then neutralized with hydrochloric acid; the ether layer was separated, the ether distilled off, and the residue dried over 50 per cent caustic potash solution. On fractionation, this yielded 18 grams of a liquid boiling at 156° at 760 mm. pressure. This liquid was 3-ethyl-2-methyl-2-pentanol. The residue from the carbinol contained other higher boiling liquids which have not yet been investigated but which will be studied in the future.

On analysis, 3-ethyl-2-methyl-2-pentanol gave the following results:

[1] Conrad and Limpach: Ann. Chem. (Liebig), 192, 153.

0.2478 gram substance gave 0.6694 gram CO_2 and 0.31 gram H_2O.

	Calculated for $C_8H_{18}O$.	Found.
C	73.85	73.69
H	13.85	13.90

Properties.—Liquid; boils at 156° under 760 mm. pressure; has a rather strong aromatic odor; and is miscible with ether, methyl alcohol, ethyl alcohol, benzene, toluene, ligroin and chloroform.

3-Ethyl-2-methyl-2-iodopropane, $(CH_3)_2C(1)CH(C_2H_5)_2$, *and its Reduction to Diethylisopropylmethane.*—For the preparation of 3-ethyl-2-methyl-2-iodopropane, 26 grams of 3-ethyl-2-methyl-2-pentanol were mixed with 2.6 grams of red phosphorus and 26 grams of iodine, and allowed to stand one hour at room temperature, after which the mixture was heated on the water bath at 60° for ten hours. The resulting iodide was decanted from the unchanged phosphorus and washed with water, but was not distilled.

It was reduced to the hydrocarbon without further purification by the following method: A 500 cc. round-bottom flask, fitted with a return condenser, was half filled with granulated zinc, the iodide was poured in, and concentrated (40 per cent) hydrochloric acid was added in small portions. The whole was heated to about 70°. At first, the heavy iodide rested on the bottom of the flask, but as the reduction proceeded the octane collected on the upper surface of the acid. This floating layer, however, still contained much unchanged iodide, which was removed by the nascent hydrogen set free at the plane of contact between the two liquid layers, the amount of zinc present being purposely kept large enough to admit of this. The action was allowed to go on about two hours, at the end of which time the octane was separated, dried over calcic chloride, then twice distilled, and a fraction boiling at 110° to 120° collected. This was treated for a week with concentrated sulphuric acid, allowed to stand several days over sodium, and finally distilled. In this way were obtained four grams of a fraction boiling sharply at 114° under 760 mm. pressure.

Analysis gave the following results:

0.1606 gram substance gave 0.4950 gram CO_2 and 0.2297 gram H_2O.

	Calculated for C_8H_{18}.	Found.
C	84.21	84.05
H	15.79	15.89

Properties.—Liquid, practically odorless, boiling at 114° under 760 mm. pressure. The specific gravity at 15° is 0.7084. The index of refraction $[\pi_D]_{25} = 1.3996$.

Second Method.

Ethyl Ethylisopropylacetacetate,

$$CH_3COC(C_2H_5)(CH(CH_3)_2)CO_2C_2H_5.$$

—Following Conrad's method[1] for the preparation of ethyl ethylacetacetate from ethyl acetacetate, sodium was dissolved in absolute alcohol and the calculated amounts of ethyl acetacetate and ethyl iodide were added. The solution was boiled until it became neutral, and the small amount of unchanged ethyl iodide was distilled off. In this alcoholic solution of ethyl ethylacetacetate an atom of sodium was dissolved, the calculated quantity of isopropyl iodide was added, the solution boiled until it was neutral, and the ethyl ethylisopropylacetacetate isolated in the usual fashion.

The fractional distillation of the product and the elimination of its impurities was rather difficult, but pure ethyl ethylisopropylacetacetate was obtained by boiling the crude product for four hours with a 10 per cent solution of caustic potash, which decomposed all other acetacetic ester derivatives, forming ketones, while only a small quantity of the principal compound was saponified. On separating the floating layer, drying with potassic carbonate, and distilling, the low boiling ketones were driven off, and after fractionating the residue twice, ethyl ethylisopropylacetacetate distilled constantly at 224° under 760 mm. pressure.

Analysis gave the following results:

0.2041 gram substance gave 0.4895 gram CO_2 and 0.1901 gram H_2O.

[1] *Loc. cit.*

	Calculated for $C_{11}H_{20}O_3$.	Found.
C	66.00	65.41
H	10.00	10.34

The yield of ethyl isopropylacetacetate was not very good, 135 grams of ethyl acetacetate giving only from 60 to 80 grams. In the above-mentioned purification by caustic potash, the same amount of material gave a few grams of acetone, about two grams of methyl-*n*-propyl ketone, a small quantity of methylisobutyl ketone, and six to seven grams of 3-ethyl-2-pentanone.

Properties of Ethyl Ethylisopropylacetacetate. — Colorless, oily liquid boiling at 224°; has a strong, rather pleasant odor like pine wood; and is miscible with ether, ethyl alcohol, methyl alcohol, benzene, toluene, glacial acetic acid and chloroform.

3-Isopropyl-2-pentanone, $CH_3COCH(C_2H_5)(CH(CH_3)_2)$. — It was found that ethyl ethylisopropylacetacetate was split into the corresponding ketone with great difficulty. By boiling with five molecules of caustic potash in ten per cent solution for sixty hours not over twenty per cent was decomposed. In some experiments the mixture was heated in an autoclave as high as 150°, but this did not better the yield, while in other experiments baric hydrate was found to act even more slowly than potassic hydrate. Increasing the concentration of the alkali brought about no practical improvement, for it caused a greater percentage of acid saponification. In the method adopted, the ester was boiled with five molecules of caustic potash (ten per cent solution) for a week and distilled with steam, and the ketone was separated, dried with calcic chloride and fractionated. The ketone collected in a fraction boiling at 145° to 165° and the unchanged ester at 220° to 225°. The fraction 145° to 165° was refractionated several times, using a long Hempel column, until the major part boiled constantly at 154° under 760 mm. It is rather difficult to get rid of small amounts of impurity which cause it to boil between 152° to 155°. The usual yield of ketone, after a week's boiling, was 25 to 30 per cent of the theoretical. The unchanged ester was recovered and treated with alkali again.

On analysis this ketone, $CH_3COCH(C_2H_5)(CH(CH_3)_2)$, gave the following results:

0.1901 gram substance gave 0.5231 gram CO_2 and 0.2204 gram H_2O.

	Calculated for $C_8H_{16}O$.	Found.
C	75.00	75.03
H	12.50	12.88

Properties.—Colorless liquid; boils at 154° under 760 mm. pressure; has a strong odor very much like camphor; and is miscible with ether, ethyl alcohol, methyl alcohol, benzene, toluene, glacial acetic acid and chloroform.

3-Isopropyl-2-pentanol, $CH_3C(OH)CH(C_2H_5)(CH(CH_3)_2)$. —This carbinol was produced from the corresponding ketone, described above, with sodium and water in presence of ether, by the method given in a previous paper for the reduction of 4-methyl-2-heptanone.[1] The fractionation of the ether residue yielded a liquid boiling at 165° to 175° which, on redistillation, boiled at 172°. This was the 3-isopropyl-2-pentanol.

The yield of carbinol was generally about ninety per cent of the theoretical (25.6 grams of ketone yielded about 23.6 grams of carbinol). No special study was made of the small amount of pinacone which occurred as a by-product.

Analysis of 3-isopropyl-2-pentanol gave the following results:

0.1002 gram substance gave 0.2708 gram CO_2 and 0.1258 gram H_2O.

	Calculated for $C_8H_{18}O$.	Found.
C	73.85	73.72
H	13.85	13.95

Properties.—Colorless, oily liquid; boils at 172° under 760 mm.; has an odor like sour bread; and is miscible with ether, ethyl alcohol, methyl alcohol, benzene, toluene and chloroform.

3-Isopropyl-2-iodopentane, $CH_3C(I)CH(C_2H_5)(CH(CH_3)_2)$, *and its Reduction to Diethylisopropylmethane.*—The preparation and reduction of 3-isopropyl-2-iodopentane was carried out by the same methods and using the same proportions as in

[1] Ber. d. chem. Ges., 40, 354.

the preparation and reduction of 3-ethyl-2-methyl-2-iodopentane already described in this paper, so it is unnecessary to give any further details. Twenty grams of this carbinol gave about 5 grams of the hydrocarbon, a yield of less than 30 per cent of the theoretical.

By this procedure an octane was obtained, which was practically odorless; boiled at 114° under 760 mm. pressure; at 15° had the specific gravity 0.7084; and the index of refraction, determined by a fine Pulfrich refractometer, $[n_D]_5$ = 1.3996. It therefore agreed perfectly in physical properties with the octane prepared by the method described in the first part of this paper, and there is no doubt that the two are identical in every respect.

The interesting analogies existing between these octanes and two others, the descriptions of which are as yet unpublished, must be reserved for a future paper.

I wish to express my indebtedness to the C. M. Warren Fund for iodine used in this research.

CAMBRIDGE, MASS.,
May 2, 1907.

[Contribution from the Texas Experiment Station.]

THE AMMONIA-SOLUBLE PHOSPHORIC ACID OF THE SOIL.

BY G. S. FRAPS.

In the course of the investigation of the phosphoric acid of the soil which is being conducted at the Texas Experiment Station, it was considered necessary to study the phosphoric acid which is dissolved by ammonia from the soil after treatment with hydrochloric acid to remove lime. This phosphoric acid, which is dissolved along with the humus of the soil, is termed by some workers humus-phosphoric acid, assumed to be in organic combination and of considerable importance.

The following experiments were designed to throw some light upon the nature and importance of ammonia-soluble phosphoric acid, as we prefer to call it.

Solubility of Mineral Phosphates in Ammonia.

It appeared desirable first to study some mineral phosphates which may occur in the soil to ascertain which one, if any, would give up its phosphoric acid to ammonia under the conditions of the extraction of humus-phosphoric acid.

Method of Work.—The quantity of phosphate containing 0.1 gram phosphoric acid was allowed to remain in contact with 2000 cc. of 4 per cent ammonia for 24 hours, being shaken from time to time.

The mixture was then filtered, 500 cc. of the filtrate evaporated to dryness, taken up with acid and water, and the phosphoric acid determined.

The amount of phosphoric acid used would correspond to 100 grams soil containing 0.1 per cent phosphoric acid in contact with 2000 cc. ammonia, or a ratio of 1 gram soil to 20 cc. ammonia. As the methods of the Association of Official Agricultural Chemists for humus require 50 cc. ammonia to 1 gram soil, the ratio of phosphoric acid to solvent is wider, and therefore the action of the solvent would be greater in the extraction of humus from the soil than in our experiment with mineral phosphates. Our results are given in the following table:

Phosphoric Acid Dissolved by Ammonia, in Percentage of Phosphoric Acid Present.

Ferric phosphate (precipitated)	100
Vivianite (ferrous phosphate)	98
Dufrenite (basic ferric phosphate)	13
Triplite (iron-manganese phosphate)	4
Wavellite (basic aluminium phosphate)	44
Variscite (aluminium phosphate)	18
Apatite	3
Phosphorite	2

Other specimens of these phosphates were examined, with similar results.

It is evident that ammonia dissolves considerable phosphoric acid from iron and aluminium phosphates, and little from the calcium phosphates.

The decomposition of ferric phosphate or vivianite by ammonia is apparent to the eye. The yellow ferric phosphate or black vivianite is converted into red ferric hydroxide, which remains suspended in the liquid.

From this experiment it appears probable that the mineral phosphates of the soil may give up some of their phosphoric acid to ammonia, and also that the inorganic phosphoric acid dissolved in the ammonia is probably of low agricultural value, being derived from iron and aluminium phosphates.

Solubility of Absorbed Phosphoric Acid.

While the preceding experiment shows that some of the ammonia-soluble phosphoric acid is probably of mineral origin, it does not prove that this is the case. We have accordingly made experiments to see if the phosphoric acid absorbed by the soil is soluble in ammonia. That is, we have determined the ammonia soluble phosphoric acid, according to the methods for humus, in soils before and after they were treated with a known quantity of potassium phosphate. An increase in the ammonia-soluble phosphoric acid (or so-called humus-phosphoric acid) can only be due to the absorbed phosphoric acid, and such an increase would be evidence that a portion of the ammonia-soluble phosphoric acid of an ordinary soil is derived from inorganic phosphates.

Method of Study.— Twenty grams soils were brought in contact with 100 cc. potassium phosphate solution containing 0.2 gram phosphoric acid. After 24 hours, the solution was poured off, the soil treated, first with 1 per cent hydrochloric acid to remove lime, then with water to remove acid, and finally with 4 per cent ammonia. The ammonia solution was made up to 1000 cc. and 100 cc. were used for the determination of phosphoric acid.

At the same time, another portion of the soil was treated with water in place of potassium phosphate, and the experiment carried out exactly as before.

None of the soils used was rich in humus. Soils 336, 341, 821, 823 and 825 contained little or no humus.

The results of the experiment are as follows:

Per cent of Ammonia-Soluble Phosphoric Acid in the Soil.

		Treated with phosphate.	Treated with water.	Gain (+) or Loss (—).
134	San Antonio loam	0.035	0.028	+0.007
326	Crawford clay	0.081	0.081	+0.000
330	Colton stony clay	0.093	0.086	+0.007
336	Lufkin fine sandy loam	0.073	0.015	+0.058
341	Susquehanna fine sandy loam (subsoil)	0.059	0.028	+0.031
829	Houston loam	0.059	0.039	+0.020
324	Houston black clay	0.065	0.039	+0.026
816	Laredo fine sand	0.036	0.025	+0.011
817	Lufkin fine sandy loam	0.036	0.029	+0.007
821	Orangeburg fine sand	0.034	0.019	+0.015
823	Orangeburg fine sandy loam (subsoil)	0.228	0.060	+0.168
825	Lufkin fine sandy loam	0.048	0.028	+0.020

It is evident that the absorbed phosphoric acid is soluble in ammonia. It follows, then, that a portion of the so-called humus-phosphoric acid is of mineral origin, and that an increase in the amount of it in the soil during the decay of vegetable matter or from other causes does not necessarily mean that a gain of organic phosphoric compound has taken place.

Soil 823, which contains practically no humus, contains as much humus-phosphoric acid, so-called, as the average of seven Minnesota soils rich in humus.

Distribution of Ammonia-Soluble Phosphoric Acid.

The ammonia-soluble phosphoric acid derived from the soil may be divided in three portions:

(1) The phosphoric acid associated with the clay held in suspension in the liquid.

(2) That precipitated with the organic matter when the liquid is neutralized with acid.

(3) The portion which remains in solution. It is a comparatively easy matter to separate the phosphoric acid into these three parts. We precipitated the clay by the addition

of ammonium sulphate in the proportion of one-half gram to 100 cc. After filtering off the precipitate and washing it several times with ammonium sulphate of the strength indicated above, the organic matter was precipitated by making the liquid slightly acid. The precipitate was collected on a filter and washed. Phosphoric acid is determined in the two precipitates and that in solution is estimated by difference, the total phosphoric acid being determined in the original solution.

The precipitation of the organic matter is not complete. Some of it remains in solution. The distribution between these groups of the phosphoric acid of some soils is given in the following table:

Percentage of Ammonia-Soluble Phosphoric Acid in the Soil.

	In clay precipitate.	In organic precipitate.	In filtrate.	Total.
741	0.005	0.021	0.042	0.068
742	0.005	0.020	0.034	0.059
743	0.008	0.019	0.016	0.043
744	0.0012	0.020	0.034	0.066
745	0.009	0.022	0.042	0.073
746	0.001	0.023	0.052	0.076
747	0.010	0.020	0.025	0.055
Average,	0.007	0.021	0.036	0.063

These soils were from Minnesota, containing 3 to 6 per cent of humus. They were kindly sent to us by Prof. Harry Snyder.

It appears that on an average 1/9 of the total ammonia-soluble phosphoric acid is in the clay precipitate, 3/9 in the organic precipitate, and 5/9 remains in the filtrate. In dealing with these small quantities, the error of analysis is of course large in comparison with the amount of phosphoric acid present. It appears from our analyses of humic acid, prepared and precipitated in quantity, that the amount of phosphoric acid which is precipitated with the organic matter is smaller than is indicated above.

Nature of Ammonia-Soluble Phosphoric Acid.

Clay Precipitate.—The phosphoric acid in the clay precipitate probably exists for the greater part in the clay particles, and is not in solution at all. This appears probable when we consider, first, that the finer portion of the soil always contains phosphoric acid, and second, that there is no reason to believe that phosphates would be precipitated from solution by addition of 0.5 per cent ammonium sulphate. There is, of course, the possibility that some of the phosphoric acid may be mechanically absorbed by the precipitate, but it is hardly likely that more than a small percentage of the total quantity present is held in this way. Otherwise we would expect a clay soil to retain a considerable portion of its ammonia-soluble phosphoric acid when treated with ammonia.

Organic Precipitate.—The phosphoric acid in the organic precipitate is very likely in organic combination.

In the first place, phosphates of iron or aluminium are soluble in acid and would hardly be precipitated when the ammoniacal liquid is made acid.

In the second place, the organic precipitate does not appear to have the power of absorbing phosphates. We dissolved 1 gram of the organic precipitate in ammonia, and added 0.02 gram phosphoric acid in the form of potassium phosphate, and reprecipitated with acid. The organic substance contained 0.0027 gram phosphoric acid and the precipitate the same quantity, which shows that no absorption had taken place. Hence it is not probable that the organic precipitate holds absorbed phosphoric acid.

We also dissolved some of the organic precipitate in ammonia, precipitated with lime, and washed. We removed lime with hydrochloric acid, dissolved the residue in ammonia, and reprecipitated with acid. The dried material was subjected to analysis. The original material contained 0.27 per cent phosphoric acid, the purified material 0.32, thus showing little change in this ingredient. We subjected 1 gram to diffusion. In 24 hours eight per cent of the organic matter passed through, but no phosphoric acid.

We conclude, from these experiments, that the phosphoric acid precipitated with the organic matter after the removal of the clay is in organic combination.

The Filtrate.—It appears probable that most of the phosphoric acid in the filtrate from the precipitation of humus with acid is in inorganic forms, although a small percentage of it may be in organic combination, since the organic precipitate is soluble in water. We have shown that the inorganic phosphoric acid absorbed by the soil is soluble in ammonia, and therefore some of the ammonia-soluble phosphoric acid must be of inorganic origin. There is no evidence that the phosphoric acid in the filtrate is in organic combination. It is probably derived from iron and aluminium phosphates.

Significance of Organic Phosphoric Acid.

We have prepared the organic precipitate from a variety of soils, and found it to contain from 0.15 to 0.54 per cent phosphoric acid. A soil containing 5 per cent humus may thus contain 0.008 to 0.022 per cent of phosphoric acid in organic combination. We found about 0.020 per cent in Minnesota soils which contain good percentages of humus.

The amount of phosphoric acid in organic combination is thus decidedly less than has been assumed from the analysis of the ammonia solution. It is hardly of any value to plants until the phosphoric acid has been released through the decomposition of the organic matter. This decomposition takes place slowly, and the most important product is available nitrogen, which is produced in about ten times the quantity of phosphoric acid released.

The organic phosphoric acid can only be regarded as a reserve store, of value according to the rate at which it decomposes. In soils containing moderate amounts of humus, it can have little importance. In soils containing large quantities of humus, it remains to be demonstrated whether phosphoric acid in this form is or is not of more value than phosphoric acid in other reserve forms.

Summary and Conclusions.

1. Mineral phosphates, especially phosphates of iron and

aluminium, give up phosphoric acid to ammonia under conditions similar to the treatment of the soil with this solvent.

2. Absorbed phosphoric acid left after treatment of the soil with acid is partly soluble in ammonia.

3. A portion of the so-called humus-phosphoric acid must be of inorganic origin; and an increase of ammonia-soluble phosphoric acid during the decay of organic matter in the soil is not evidence that there is a gain of organic phosphoric acid.

4. About 1/9 of the ammonia-soluble phosphoric acid of some Minnesota soils is associated with the clay, 1/3 is associated with the organic matter, and 5/9 remains in solution.

5. The phosphoric acid associated with the organic matter does not diffuse and the amount of it does not increase when the organic matter is precipitated in the presence of phosphoric acid, nor does it decrease when the organic matter is dissolved, precipitated with lime, the lime removed, the precipitate dissolved in ammonia, and reprecipitated. We conclude that the phosphoric acid is in organic combination.

6. The phosphoric acid with the clay is probably not in solution; that in the filtrate is probably for the most part of inorganic origin, derived from iron and aluminium phosphates.

7. The organic phosphoric acid is in much smaller quantity than has been believed to be the case, and therefore of less agricultural significance.

The author wishes to acknowledge the assistance of Messrs. N. C. Hamner and S. E. Asbury, who performed the analytical work.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

STUDIES IN CATALYSIS.[1]

V. THE CATALYSIS OF IMIDOESTERS.

By William McCracken.[2]

When the hydrochloride of an imidoester is dissolved in water, it is rapidly decomposed by the water into ammonium chloride and an acid ester according to the formulation,

[1] Articles I.–IV., This Journal, **39**, 29, 166, 402, 437.

[2] This work was begun in 1898–9 (This Journal, **26**, 309), completed, written and accepted as a dissertation in 1905 and sent to the editor in September, 1907.

$$C_6H_5C(:NH_2Cl)OC_2H_5 + H_2O \longrightarrow C_6H_5COOC_2H_5 + NH_4Cl \quad (1).$$

It was early observed that the decomposition appeared to proceed fastest with the salts of those imidoesters which presumably form the weaker bases; for instance, the hydrochloride of ethyl imido-*m*-nitrobenzoate is decomposed very much more rapidly than that of ethyl imidobenzoate. From my own preliminary experiments I found that in one hour 17.44 per cent of the latter was decomposed, while of the former, in the same time and under the same conditions, 8.17 per cent was changed. As all the imidoesters are weak bases and their salts are consequently more or less hydrolyzed by water in proportion to the weakness of the base,

$$C_6H_5C(:NH_2Cl)OC_2H_5 + H_2O \rightleftarrows C_6H_5C(:NH_2OH)OC_2H_5 + HCl \quad (2),$$

it appeared that there might be some connection between the two facts—the relative weakness of the base, as revealed in (2), and the relative velocity of the decomposition shown in (1).

The study of the decomposition of imidoester salts by water was undertaken by me at the suggestion and under the direction of Professor Stieglitz, with the particular object of ascertaining what component of the hydrolyzed mixture, salt or free base, suffers decomposition by water into ester and ammonia, and of determining whether there is any general relation between the velocity of the decomposition of the salts and the affinity constant of the bases, as has just been explained. The study forms part of the investigations on catalysis carried out in this laboratory, and the theoretical and mathematical presentation of the problems involved will be found in the recent papers by Professor Stieglitz[1] on this subject.

I. THE METHODS OF ANALYSIS.

The experimental treatment of the subject under investigation resolved itself into two lines of work. It was necessary, first, to devise methods for following the velocity of reaction

[1] THIS JOURNAL, *loc. cit.*

(1) quantitatively at a given temperature, and, in the second place, to determine the hydrolysis constants of the salts used. The course of reaction (1) was followed by two different analytical methods. Imidoesters are readily converted into bromimidoesters[1] by the action of hypobromous acid or of bromine and alkalis:

$$C_6H_5C(:NH)OC_2H_5 + HOBr \rightarrow C_6H_5C(:NBr)OC_2H_5 + H_2O \quad (3).$$

The resulting bromimidoesters are compounds which are difficultly soluble in water and readily extracted by organic solvents; and they are also very readily reduced back to imidoesters by the action of hydriodic acid, iodine being liberated quantitatively according to the formulation

$$C_6H_5C(:NBr)OC_2H_5 + 2HI \rightarrow C_6H_5C(:NH_2Br)OC_2H_5 + 2I \quad (4).$$

These reactions formed the basis of the first analytical method used; at certain time intervals a measured amount, 25 cc. as a rule, of the solution under investigation was brought into a 250 cc. "Squibb" separatory funnel, 15 cc. of carbon tetrachloride was added, then excess of bromine, and finally 10 per cent sodium hydroxide with vigorous shaking, until the carbon tetrachloride retained but a slight greenish tint. The carbon tetrachloride containing the bromimidoester was then filtered through a paper wet with carbon tetrachloride and the solution extracted again with 10 and 5 cc., respectively, of carbon tetrachloride. To the extracts collected in a glass-stoppered bottle were then added 15 cc. of a 25 per cent solution of potassium iodide and 10 cc. of dilute hydrochloric acid, and the free iodine titrated with N/10 thiosulphate.

The only difficulty met with in the application of the method consisted in the determination of the point at which the excess of bromine used in converting the imidoester into the bromimide is just removed by the addition of alkali, considerable excess of alkali reversing reaction (3) and resulting in a loss of bromimide. Prolonged practice with weighed quan-

[1] Stieglitz: THIS JOURNAL, 18, 761 (1896).

tities of the imidoester salt made it possible to determine with considerable accuracy, by the tint of the carbon tetrachloride layer, at which point the excess of bromine is removed without a loss of bromimidoester. The following results of blank experiments with the hydrochloride of ethyl imidobenzoate show the degree of accuracy of the method:

Salt used, gram.	cc. N/10 thiosulphate required.	cc. N/10 thiosulphate calculated.
0.2415	26.19	26.15
0.1144	12.37	12.33
0.2080	22.26	22.43

The second analytical method, developed in the investigations of Stieglitz and Derby,[1] is far easier and more reliable in execution than the bromine method and eliminates the personal factor involved in judging a tint. The degree of accuracy is shown by the blank experiments of Stieglitz and Derby, as well as by the following determinations made by myself with imidoester salts which they did not use.

The Hydrochloride of Isoamyl Imidobenzoate.

Substance used, gram.	cc. N/10 NaOH calculated.	cc. N/10 NaOH found.
0.2360	10.38	10.37
0.2947	12.95	12.95
0.2277	10.01	10.03

The Hydrochloride of Isobutyl Imidobenzoate.

Substance used, gram.	cc. N/10 NaOH calculated.	cc. N/10 NaOH found.
0.2520	11.80	11.82
0.2454	11.49	11.47

The Hydrochloride of Ethyl Imido-p-toluylate.

Substance used, gram.	cc N/10 NaOH calculated.	cc. N/10 NaOH found.
0.3630	18.18	18.13
0.3214	16.10	16.02

Analyses were also made of the hydrochloride of isoamyl imidobenzoate in the presence of added ammonium chloride to see if it affected the method. The following results were

[1] THIS JOURNAL, **39**, 437.

obtained, 0.1 and 0.5 equivalents, respectively, of ammonium chloride being used:

Substance used, gram.	cc. N/10 NaOH calculated.	cc. N/10 NaOH found.
0.2301	10.11	10.18
0.2280	10.02	10.03

These results show that the presence of ammonium chloride does not affect the method.

The reliability of the analytical method used with each salt of an imidoester was tested in every instance with the salt itself.

The experimental determinations of the hydrolysis constants of equation (2) and the affinity constants of the imidoesters were made by the conductivity method of Walker[1] and of Bredig,[2] the degree of hydrolysis being ascertained by the equation

$$x = \frac{M_{obs} - \Lambda_s}{\Lambda_{HCl} - \Lambda_s},$$

where x is the percentage of free base and acid liberated by hydrolysis, M_{obs} is the observed molecular conductivity, and Λ_s and Λ_{HCl} are the molecular conductivities of the non-hydrolyzed salt and of hydrochloric acid, respectively, for the concentration used.[3] Since a solution of the salt (equation 2) is continually decomposing according to (1) from the first moment that the water touches it, it was necessary to ascertain the conductivity, M_{obs}, for the unchanged solution ($t = 0$) from the results of a series of readings made at stated time intervals. The conductivity changed slowly in most cases under investigation and a simple method of extrapolation, based on the observed conductivities without regard to the velocity constants[4] of reaction (1), was found to be sufficiently accurate. The method of extrapolation used will be explained in connection with some of the data found in the next part. In two or three cases (ethyl imido-*m*-nitro-

[1] Z. physik. Chem., **4**, 319 (1889).
[2] *Ibid.*, **13**, 289 (1894).
[3] Stieglitz and Derby: THIS JOURNAL, **31**, 449 (1904).
[4] Stieglitz and Upson: THIS JOURNAL, **31**, 458 (1904).

benzoate and the imidoesters of phenylacetic acid), the velocity of decomposition proved to be so great that a double method of extrapolation had to be resorted to (p. 605) in order to find M_{obs}, and the constants obtained in some cases are considered to be, at best, approximations.

The molecular conductivities, Λ_s, of the nonhydrolyzed salts were measured by Bredig's method, the conductivity being determined in the presence of sufficient free base added to the salt solution to overcome the hydrolysis, without, at the same time, having enough free base present to affect the measurement. In this case, too, decomposition according to (1) occurred continually and the values for Λ_s were found by extrapolation from a series of readings, exactly as in the case of M_{obs} for the hydrolyzed salt.

From the degree of hydrolysis, x, the hydrolysis constants, K_{hydr}, and the affinity constant, k_{base}, were calculated in the usual way according to the Walker-Arrhenius equation for hydrolyzed salts:

$$\frac{C_{salt}}{C_{base}\,C_{acid}} = \frac{k_{base}}{k_w} = K_{hydr} \qquad (7),$$

where C_{salt}, C_{base} and C_{acid} signify the concentrations of salt, base and acid in gram molecules per liter, and k_w is the ion product for water (1.2×10^{-14} at 25°).[1] If one gram molecule of salt is used in V liters, we have

$$\frac{V(1-x)}{x^2} = \frac{k_{base}}{k_w} = K_{hydr} \qquad (8).$$

II. EXPERIMENTAL PART.

1. *The Hydrochloride of Ethyl Imidobenzoate.*

The hydrolysis constant for the hydrochloride of ethyl imidobenzoate and the affinity constant for the base were determined by Stieglitz and Derby[2] as follows:

$$K_{hydrolysis} = 9.1 \times 10^5.\ k_{base} = 10.9 \times 10^{-9}.$$

The velocity of the decomposition of the salt by water was determined by me in a series at 25° (±0.01).[3]

[1] Van't Hoff's "Lectures on Theoretical and Physical Chemistry," 1, page 133.
[2] *Loc. cit.*
[3] In a few earlier experiments the variations were sometimes 0°.05 to 0°.1. The exact temperature will be given in each case.

In the following table, columns 1 and 5 give the time in minutes, and columns 2 and 6 the cc. of N/10 thiosulphate required for 25 cc. of the salt solution. These volumes are proportionate to the concentration ($C - x_t$) at any moment t and are used in calculating the constant according to the equation for a monomolecular reaction,[1]

$$k_{salt} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (9).$$

Columns 3 and 7 give the constants calculated according to this equation. In all the experiments the concentration of the salt was 0.05 molar.

Table I.

t.	cc. N/10 thiosulphate.	$434.3 \times k_{salt}$.	Temp.	t.	cc. N/10 thiosulphate.	$434.3 \times k_{salt}$.	Temp.
0	25.00	1.34		60	20.57	1.41	
60	20.78	1.36	25°.1	120	16.77	1.45	25°
120	17.16	1.35		180	14.16	1.37	
180	14.26	1.39		240	11.65	1.38	
240	11.60						
60	20.60	1.40		180	13.58	1.41	25°.08
120	16.83	1.43	25°.05	360	8.09	1.36	
180	14.17	1.37					
240	11.80	1.36					
60	20.63	1.39		180	14.15	1.41	25°.08
120	16.92	1.41	25°.08	360	8.27	1.35	25°.08
180	14.39	1.33					
240	11.88	1.35					

Mean: $434.3\ k_{salt} = 1.384$; $k_{salt} = 0.00319$.

These results show that the velocity of the reaction is proportionate to the concentration of the salt present in the solution of the hydrolyzed imidoester salt (equation 2). The velocity constants, k_b, were also calculated for a reaction supposed to proceed with a velocity proportionate to the concentration of the free base[2] present at any moment according to the combined equations (1) and (2). If the reaction

[1] The salt is so little hydrolyzed according to (2) that k represents almost exactly the velocity of decomposition as being proportionate to the concentration of the salt. See Stieglitz: *Loc. cit.*

[2] See Stieglitz and Upson: THIS JOURNAL, 31, 458 (1904).

velocity of the equation (1) were proportionate to the concentration of the free base, we would have[1]

$$k_b = \frac{2}{t_2 - t_1}\sqrt{\frac{K_{hydr}}{V}}\left[\sqrt{1 - x_1} - \sqrt{1 - x_2}\right] \qquad (10),$$

in which K_{hydr} is the hydrolysis constant of equation (2) and V the volume in which one gram molecule of salt is dissolved.

The first two series of Table II. give the values for k_b calculated according to this equation for the decomposition of the salt in a 0.05 molar solution. As was to be expected, the values are not constant. As a farther test of this point, the velocity of decomposition was also determined in solutions of the imidoester salt containing a known excess of free base, thus permitting of a greater variation in the concentrations of the base. If the velocity of decomposition of an imidoester into ammonia and an acid ester were proportionate to the concentration of the free base present, then for a mixture of the salt and an added excess of free base we would have

$$\left\{ k_{base} = \frac{1}{K_v(t_2 - t_1) + (1 - s - K_v)\ \text{log nat}\ \dfrac{\sqrt{R - 4K_v x_2} + (1 - s - K_v)}{\sqrt{R - 4K_v x_1} + (1 - s - K_v)}} \right\} \qquad (11),$$

in which $K_v = V/K_{hydrolysis}$ and $R = (1 - s + K_v)^2 + 4K_v s$. One gram molecule of imidoester (base and salt) is used in V liters; s gives the percentage of one gram molecule of salt present; $1 - s$, the percentage of one molecule of base. The volume V was always 20 liters in these experiments. The last two series of Table II. give the results.

Table II.

t.	cc. N/10 thiosulphate.	k_{base}.		t.	cc. N/10 thiosulphate.	k_{base}.	
60	20.78	0.63		180	14.14	0.149	25°.04
120	17.16	0.61	25°.1	360	8.21	0.115	$s = 0.984$
180	14.26	0.58	$s = 1$				
240	11.60	0.53					
60	20.60	0.66		180	14.37	0.0481	25°.04
120	16.83	0.64	25°.05	360	8.25	0.0384	$s = 0.950$
180	14.17	0.59	$s = 1$				
240	11.80	0.47					

[1] Stieglitz: *Loc. cit.* The formula is simplified from the rigorous expression as explained in the above paper.

It is certain, therefore, that the reacting substance in the formation of an ester and ammonia is not the free base, as was at one time thought possible, but rather the salt or its positive ion. This conclusion was confirmed by the results obtained in the presence of an added excess of hydrochloric acid. Although a small excess of acid practically eliminates all the free base formed by hydrolysis, owing to the large value of the hydrolysis constant, the velocity of the reaction remains practically unchanged in the presence of the small excess of acid.

A larger excess of acid reduces the velocity considerably. As in dilute solutions the salt is very largely dissociated into its ions, it was thought from the beginning that the real reacting substance is the positive ion only[1] and that the true velocity constant would show a reaction proceeding directly proportionate only to the concentrations of the positive salt ion present and not to the total salt concentrations. The addition of an excess of acid, by increasing the total electrolyte concentration, decreases the degree of ionization according to Arrhenius' principle of isohydric solutions. When this work was first carried out it was intended to assume provisionally in our calculations that the degree of ionization of the hydrochloride of ethyl imidobenzoate would correspond approximately to that of ammonium chloride in similar concentrations. Since then Dr. Schlesinger[2] has determined directly the degrees of ionization of the imidoester salts and we are indebted to him for the use of his values for α in the following calculations. Schlesinger has shown, in the work on the velocity of decomposition of the imidoester salts in solutions of varying concentrations, that, the velocity being put proportionate to the concentration of the positive ester ions, there is an accelerating "salt effect" corresponding to the like effect of electrolytes on the catalysis of cane sugar, methyl acetate, etc. We have included the consideration of this effect also in the analysis of the experimental data on the velocity of decomposition of ethyl imidobenzoate in the

[1] *Vide* Stieglitz.

[2] See a later article in THIS JOURNAL.

presence of an excess of hydrochloric acid. In Table III. are given the data of these determinations, all of which were carried out with 0.05 molar ethyl imidobenzoate and varying amounts of hydrochloric acid. The first three columns have the same significance as in Table I. In columns 4 and 8 the excess of acid used is given in moles per liter, and the exact temperature for each experiment is given in the same column. 25 cc. were used for each titration, and when $t = 0$ these require 25 cc. N/10 thiosulphate. The constants are calculated according to the logarithmic function (equation 9),

$$K = \frac{1}{t} \log \text{nat} \frac{25}{v_t},$$

in which v_t represents the cc. thiosulphate used at the moment t.:

Table III.

t.	cc. N/10 thiosulphate.	$434.3 \times k_{salt.}$	Acid (temp.).	t.	cc. N/10 thiosulphate.	$434.3 \times k_{salt.}$	Acid (temp.).
180	14.08	1.385	0.05	60	21.00	1.260	
360	7.97	1.380	25°.00	120	17.78	1.235	0.25
180	14.15	1.373	0.05	180	15.00	1.233	25°.03
360	8.04	1.370	25°.05	240	12.61	1.240	
180	14.42	1.330	0.10	60	21.37	1.133	0.5
360	8.46	1.308	25°.00	120	18.21	1.147	25°.05
180	14.34	1.341	0.10	180	15.67	1.127	
360	8.37	1.320	25°.01	240	13.46	1.122	
120	17.62	1.267	0.25	60	21.95	0.942	
180	14.94	1.241	25°.03	120	19.31	0.935	1.00
240	12.71	1.225		180	17.00	0.931	25°.00
				240	15.17	0.904	

In Table IV. (p. 598) the analysis of the data is given. Column 1 in the table gives the moles of hydrochloric acid used in excess with the 0.05 molar solution of ester salt. In column 2 are given the estimated concentrations of the imidoester solutions whose degree of ionization would correspond to that of the imidoester salt as affected by the presence of the added acid; these concentrations are calculated on the basis of the theory of isohydric solutions, that the salt and acid may be supposed to share the water present in such proportions that the concentration of the common ion $(\overline{Cl})$ becomes the

same for the acid and the salt in their respective parts of the solution;[1] then, when such solutions are mixed in any proportions there is practically no change in the degree of ionization of the electrolytes. In making this estimation, the difference in the degree of ionization of the acid and salt in equimolar solutions was taken into consideration, that of the salt (Schlesinger) being unusually low. In line 2, for instance, if the salt and acid ionized approximately equally, the ionization of the salt would be referred, as usual, to a salt solution equimolar to the total electrolyte concentration (0.05 + 0.05 or 0.1 molar), but the difference in the degree of ionization of the salt and the acid makes it necessary to consider the water divided in about the ratio of 0.53 part for the acid and 0.47 part for the salt, and (0.05/0.47) gives 0.106 as the concentration of the isohydric salt solution. The correction here is very slight but, as will be seen in the table, it is quite considerable for the stronger acid solutions; for 0.5 molar acid, for instance, we have a partition of the water in about the ratio 0.94:0.06 (instead of 0.91 to 0.09) to secure isohydric solutions, and the salt solution is then 0.8 molar instead of 0.55.

In column 3, the degree of ionization of the salt is given corresponding to the molar concentration given in column 2; the values are obtained by interpolation from Dr. Schlesinger's determinations.

In column 4, the observed velocity constant, k_{salt}, is given, as reported in Table III., for each experiment. In column 5, the velocity of the reaction is referred to the concentration of the positive salt ion according to the equation

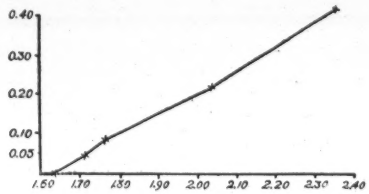
$$K_{ion} = \frac{k_{salt}}{\alpha} \qquad (13).$$

The values in this column show very markedly the large accelerating effect of the hydrochloric acid, or, rather, of its ions.[2] If the action is really subject to this effect, the effect

[1] Arrhenius: Z. physik. Chem., **2**, 286 (1888).

[2] This accelerating "salt effect," it may be recalled, is generally ascribed to the influence of the salt ions on the dissociation or active mass of water [Arrhenius: Z. physik. Chem., **1**, 126 (1887); **4**, 235 (1889); and Euler: *Ibid.*, **33**, 348 (1900)] which enters into the action under investigation, as shown in equation (1). See Stieglitz: THIS JOURNAL, articles I. and II., *loc. cit.*

should be, as usual, directly proportionate[1] to the concentration of the ions of the acid;[2] in other words, the velocity should be a rectilinear function of these concentrations. The accompanying diagram shows that, as a matter of fact, if we plot the concentrations of the acid ions ($m \times \alpha_{HCl}$ of columns 1 and 6 in the table) as ordinates and the velocities K_{ion}, *i. e.*, K_{salt}/α, as abscissas we do get a very nearly straight



line. By taking, from the diagram, the acceleration as $\frac{0.73}{0.42 \times 1.63}$ or 1.07 per gram ion of hydrogen (the concentration of hydrogen ions is proportionate, of course, to the total concentrations of ions obtained from hydrochloric acid) we can calculate, for each experiment, the velocity with which it ought to proceed if our theory is correct. The observed velocity, 434.3 k_{salt}, should correspond to the calculated velocity, 434.3 $k_{salt\ calc.}$, found as follows:

$$434.3\ k_{salt\ calc.} = \frac{1.384 \times \alpha_{salt} \times (1 + 1.07\ m_{HCl} \times \alpha_{HCl})}{0.846} \quad (13),$$

in which 1.384 is the velocity in absence of any acid; 0.846, the degree of ionization for this condition; α_{salt}, the degree of ionization of the salt given in column 3; m_{HCl}, the concentration of the added acid (column 1); and α_{HCl}, the degree of ionization of the acid as calculated from the conductivities for concentrations equal to the total electrolyte concen-

[1] Arrhenius: *Loc. cit.*

[2] The effect of the ions of the 0.05 mole of salt present (see Schlesinger's paper) is so small, compared with that of the acid, that it was neglected.

trations. Column 6 gives α_{HCl}, and column 7 the calculated constant, $434 \cdot 3\ k_{salt\ calc.}$

Table IV.

1 *macid.*	2 *Est salt.*	3 $100\ \alpha_{salt.}$	4 $434 \cdot 3\ k_{salt}$	5 $\frac{434 \cdot 3\ k_{salt}}{\alpha_{salt.}}$	6 $100\ \alpha_{HCl.}$	7 $\frac{434 \cdot 3 \times}{k_{calc\ salt.}}$
0.00	0.05	84.6	1.384	1.63	0.00	1.384
0.05	0.106	80.0	1.372	1.72	91.4	1.374
0.05	0.106	80.0	1.383			
0.10	0.167	74.7	1.319	1.77	90.9	1.340
0.10	0.167	74.7	1.330			
0.25	0.4	61.0	1.242	2.04	87.5	1.231
0.25	0.4	61.0	1.244			
0.50	0.8	(48.0)	1.132	2.36	84.3	1.139

The comparison of the last column, $k_{calc\ salt}$, with the fourth column, giving the experimental values for k_{salt}, shows how close the agreement is between the two values in all the concentrations used.

We may conclude, therefore, that this series of experiments confirms the result established by Stieglitz and Schlesinger that the decomposition of salts of imidoesters according to the equation (1) is a reaction of the positive salt ions, proceeding proportionate to their concentrations, and subject to an acceleration by the so-called "salt effect" proportionate to the electrolyte used,[1] presumably owing to an effect on the active mass of water, the other agent in the action (see equation 1). The reaction should, therefore, more properly be represented as follows:[2]

$$C_6H_5C(\overset{+}{N}H_2)OC_2H_5 + HOH \longrightarrow C_6H_5CO_2C_2H_5 + \overset{+}{N}H_4 \quad (1').$$

2. The Hydrochloride of Isobutyl Imidobenzoate.

The hydrolysis constant (equation 2) for isobutyl imidobenzoate was determined by conductivity measurements of the salt solution in the absence and presence of a slight ex-

[1] A more extensive, rigorous investigation of the "salt effect" is being carried out by Miss Edith Barnard. The above results are merely preliminary.

NOTE: Dr. McCracken's article was written in 1905, Dr. Barnard's work completed in 1907.—J. S.

[2] Stieglitz: *Loc. cit.*

cess of the free base. As the salt undergoes continuous change in the solution, the conductivities for $t = 0$ were ascertained by a process of extrapolation which will be illustrated by the data for the experiments with 1/32 and 1/64 molar salt solutions. For the sake of brevity, the like data for all later experiments will be omitted.

The measurements were made with a Kohlrausch bridge at 25° (±0.01) in an Arrhenius cell. The water used had a specific conductivity of 4×10^{-6}, for which a correction was made only in the neutral solutions in the presence of the added base, but not in the case of the acid-reacting hydrolyzed salt solutions. The conductivities are given in reciprocal ohms.

In the following table, V., we have in columns 1 and 5 the time in minutes; in columns 2 and 6, the observed specific conductivities; in columns 3 and 7, the difference in these for 5 minute intervals. In columns 4 and 8 the extrapolated values for the *original* specific conductivities are given.

Table V.

1/32 molar.

t.	$10^6 \times \kappa$.	Δ.	$10^6 \times \kappa_0$.	t.	$10^6 \times \kappa$.	Δ.	$10^6 \times \kappa_0$.
0	....	..	(2741)	15	2826	23	2740
5	2769	..	2741	20	2852	26	2738
10	2803	34	2746	25	2883	31	2740
					Mean,	28.5	2741

The mean specific conductivity calculated for $t = 0$ is 0.002741: the molecular conductivity is therefore 87.7.

2. 1/64 molar.

t.	$10^6 \times \kappa$.	Δ.	$10^6 \times \kappa_0$.	t.	$10^6 \times \kappa$.	Δ.	$10^6 \times \kappa_0$.
0	....	..	(1442)	15	1482	13	1442
5	1455	14	1442	20	1497	15	1443
10	1469	..	1445	25	1509	12	1441
					Mean,	13.5	1442

In Table VI. a summary of the data is given for the estimation of $K_{hydrolysis}$. The calculation is made according to the Arrhenius-Walker method.[1]

[1] Page 591.

Table VI.

V.	M_v.	Λ_v.	$100x$.	$10^{-5}\,K_{hydrolysis}$.
32	87 70	85.82	0.612	8.5
32	87.25	85.82	0.466	15.0
64	92.29	89.73	0.828	9.3
64	92.16	89.73	0.786	10.3
128	97.40	93.47	1.28	7.8
256	100.40	95.82	1.49	11.3

Mean: $K_{hydrolysis} = 10.4\times10^{5}$; $k_{base} = 12.5\times10^{-9}$.

In Table VII. are given the results of the determination of the velocity of decomposition of the hydrochloride by water at 25° (±0.01°). The constant, k_{salt}, is calculated according to equation (9). 25 cc. of the salt solution was used for each titration. V gives the volume containing 1 gram molecule of salt.

Table VII.

1. $V = 30$.

t.	cc. N/10 NaOH.	$434.3\times k_{salt}$.	t.	cc. N/10 NaOH.	$434.3\times k_{salt}$.
0	8.33	....	200	4.51	1.33
10	8.02	(1.65)	260	3.80	1.31
40	7.40	1.29	320	3.19	1.30
140	5.40	1.34			

Mean: 434.3 $k = 1.315$; $k = 0.00303$.

2. $V = 20$.

t.	cc. N/10 NaOH.	$434.3\times k_{salt}$.	t.	cc. N/10 NaOH.	$434.3\times k_{salt}$.
0	12.50	....	130	8.498	1.29
10	12.13	1.31	160	7.76	1.29
40	11.10	1.29	190	7.14	1.28
70	10.19	1.27	340	4.58	1.28
100	9.28	1.29	370	4.20	1.28

Mean: 434.3 $k = 1.287$; $k = 0.00296$.

For k_{ion} we have $k_{ion} = k_{salt}/\alpha$, or, for the 1/30 molar solution,[1]

$$k_{ion} = \frac{0.001315}{0.4343\times0.876} = 0.003456,$$

and for the 1/20 molar solution

$$k_{ion} = \frac{0.001287}{0.4343\times0.846} = 0.003502.$$

[1] α was taken to be the same for the isobutyl ester as found by Schlesinger for the ethyl ester.

3. The Hydrochloride of Isoamyl Imidobenzoate.

The following table, VIII., gives the data for the calculation of the hydrolysis constant:

Table VIII.

V.	M_v.	Λ_v[1].	100x.	10^{-5} $K_{hydr.}$
32	88.46	86.7	0.579	9.6
64	91.90	89.6	0.745	11.5
128	95.23	92.41	0.912	15.2
256	98.84	95.33	1.14	19.4

Mean, 14.0×10^5.

For the affinity constant we have $k_{base} = 17 \times 10^{-9}$.

In Table IX. we have the results of the determinations of the velocity of decomposition of the hydrochloride in water at 25° (±0.01°). The values in this table are obtained in the same way as those in Table VII., and the columns have the same significance.

Table IX.

1. $V = 20$.

t.	cc. N/10 NaOH.	434.3 × $k_{salt.}$	t.	cc. N/10 NaOH.	434.3 × $k_{salt.}$
0	12.5	....	120	8.78	1.27
10	12.1	(1.41)	180	7.40	1.27
60	10.49	1.27	240	6.09	1.30

Mean: 434.3 $k = 1.278$; $k = 0.00294$.

2. $V = 20$.

t.	cc. N/10 NaOH.	434.3 × $k_{salt.}$	t.	cc. N/10 NaOH.	434.3 × $k_{salt.}$
0	12.50	....	160	7.80	1.28
10	12.09	(1.45)	199	6.98	1.27
40	11.08	1.31	320	4.92	1.27
80	9.76	1.34	360	4.32	1.28
120	8.74	1.29	400	3.94	1.25

Mean: 434.3 $k = 1.287$; $k = 0.00296$.

3. $V = 10$.

t.	cc. N/10 NaOH.	434.3 × $k_{salt.}$	t.	cc. N/10 NaOH.	434.3 × $k_{salt.}$
0	25.00	....	174	15.22	1.24
14	24.15	(1.08)	214	13.62	1.23
54	21.44	1.24	334	9.82	1.22
94	19.19	1.22	374	8.71	1.22
134	17.05	1.24	404	8.03	1.22

Mean: 434.3 $k = 1.229$; $k = 0.00283$.

[1] N/80 free base was used.

For k_{ion} we have, for the 1/20 molar solution, $k_{ion} = 0.003491$. For the 1/10 molar solution, $k_{ion} = 0.003505$.

4. The Hydrochloride of Ethyl Imido-p-toluylate.

In the next table will be found the calculations of the hydrolysis constant of this substance at 25° (±0.01).

Table X.

V.	M_v.	Λ_v.[1]	100x.	10^{-5} $K_{hydr.}$
32	89.12	88.00	0.597	8.9
64	93.50	91.58	0.625	16.3
64	93.31	91.58	0.564	20.0
128	96.95	94.42	0.824	18.7
128	97.09	94.42	0.873	16.8
256	99.02	95.21	1.241	16.43
256	98.87	95.21	1.196	17.7
		Mean,		16.4×10^{5}

For this compound, therefore, $k_{base} = 19.7 \times 10^{-9}$.

In Table XI. are given the results of the determinations of the velocity of decomposition of the hydrochloride in water at 25° (±0.01).

Table XI.

1. $V = 20$.

t.	cc. N/10 NaOH used.	434.3 × k_{salt}.	t.	cc. N/10 NaOH used.	434.3 × k_{salt}.
0	12.50	....	195	9.42	0.630
10	12.28	(0.771)	315	7.93	0.627
40	11.75	0.672	1305	1.80	0.645
70	11.26	0.648			

Mean: 434.3 $k = 0.644$; $k = 0.00128$.

2. $V = 30$.

t.	cc. N/10 NaOH used.	434.3 × k_{salt}.	t.	cc. N/10 NaOH used.	434.3 × k_{salt}.
0	8.33	...	330	5.07	0.654
10	8.20	(0.684)	1360	1.07	0.655
190	6.27	0.649			

Mean: 434.3 $k = 0.653$; $k = 0.00150$.

For the 1/20 molar solution, we have $k_{ion} = 0.00175$.
For the 1/30 molar solution, $k_{ion} = 0.00172$.

[1] N/80 free base was used.

5. The Hydrochloride of Methyl Imido-o-toluylate.

Attempts were first made to prepare the ethyl ester by the usual method from the nitrile by the action of hydrogen chloride and alcohol, but with no more success than Pinner[1] had. The following three experiments were carried out:

1. Equal molecular weights of the nitrile, alcohol, and dry hydrogen chloride were used.

2. Equal molecular weights of the nitrile and acid, and ten molecules of alcohol.

3. A gram of the nitrile was dissolved in ten molecules of alcohol, and the mixture saturated with dry hydrochloric acid gas.

In none of the experiments was a trace of the imidoester formed.

A second attempt was made to prepare the ethyl ester by ethylating the silver salt of the acid amide. The amide was made by heating for several hours a mixture of *o*-tolyl nitrile and hydrogen peroxide,[2] and by heating a mixture of the nitrile and concentrated sulphuric acid. The latter method proved the better. The following method of converting the amide into the silver salt gave the best results: The amide was dissolved in hot dilute alcohol and the silver nitrate and sodium hydrate added simultaneously, drop by drop. In this way, a voluminous, white precipitate of the silver salt was obtained, which decomposed slightly on being washed with cold water. The analyses of the body gave the following results:

I. 0.1004 gram substance gave 0.0455 gram Ag.
II. 0.3099 gram substance gave 0.1401 gram Ag.

	Calculated for $C_8H_8ON.Ag$.	Found I.	Found II.
Ag	44.61	44.82	45.20

All attempts to alkylate this salt with ethyl iodide failed. In no case did the ethereal extract give a trace of the hydrochloride when dry hydrogen chloride was passed through it. Methyl iodide was then tried. It was added to a mixture

[1] Pinner: Imidoaether, p. 63.
[2] Radzewski: Ber. d. chem. Ges., **18**, 355 (1895).

of the silver salt and a little ether, and the mixture allowed to stand from 24 to 48 hours. It was then extracted with ether, and when dry hydrogen chloride gas was passed through the extract, the hydrochloride of methyl imido-*p*-toluylate separated out in small, white flakes. A second treatment with methyl iodide gave a little more of the substance, but the total yield was small. The hydrochloride crystallizes in small, white flakes, and has a very agreeable cinnamonlike odor. On being heated rapidly it decomposes with effervescence and the resulting gas burns with a green flame. The solid residue (the amide) melts at 138°. If heated slowly, the salt decomposes without visible effervescence. Analyzed for chlorine, the salt gave the following results:[1]

0.149 gram substance required 8.07 cc. N/10 NaOH.

	Calculated for $C_9H_{12}NOCl$.	Found.
Cl	19.13	19.23

In Table XII. are given the data for the calculation of the hydrolysis constant of this compound at 25° (±0.01).

Table XII.

V.	*Mv.*	Δ_v.	100*x*.	10^{-5} $K_{hydr.}$
32	99.01	94.8	1.409	1.6
64	104.8	98.0	1.90	1.75
128	109.6	101.2	2.80	1.6
256	113.1	103.3	3.01	2.75
			Mean,	1.90×10^5

$k_{base} = 2.3 \times 10^{-9}$.

In Table XIII. will be found the results of the determinations of the velocity of decomposition of the hydrochloride in water at 25° (±0.01).

Table XIII.

1. $V = 32$.

t.	cc. N/10 NaOH used.	$434.3 \times k_{salt.}$
0	7.81	....
1001	2.55	0.486
1419	1.61	0.483

$k = 0.00111$ and $k_{ion} = 0.001276$.

[1] The titration was made with phenolphthalein by the method described by Miss Barnard (see a later paper).

6. The Hydrochloride of Ethyl Imidophenylacetate.

On account of the rapid decomposition of this salt in water, a double method of extrapolation was resorted to in order to find M_v and Λ_v at $t = 0$. An explanation of the method of extrapolation for the 1/32 molar solution will be given in the following table, XIV. The temperature of the experiments was 25° (±0.02):

Table XIV.

1.32 molar solution.

t	$10^6 \times K$.	Δ.	$\Delta 5$ min.	$\Delta\Delta$.	$10^6 \times \kappa_0$.
0	....	...	(353)	..	(2816)
5	3169	125	312	29	...
7	3294	170	283	21	...
10	3464	105	262	74	...
12	3569	113	188		...
15	3682				...
			Mean,	41	

In Table XV. will be found the data for the determination of the hydrolysis constant at 25° (±0.01).

Table XV.

V.	M_v.	Λ_v[1].	$100x$.	$10^{-5} K_{hydr.}$
32	90.11	85.56	1.15	2.4
64	95.76	91.01	1.55	2.6
128	98.11	93.19	1.60	5.0
			Mean,	3.3

$k_{base} = 4 \times 10^{-9}$.

In the following table, XVI., are given the values of the determinations of the velocity of decomposition, referred to the concentration of the salt (equation 9) and also to the concentration of the free base (equation 10), for a 0.05 molar solution at 0° (±0.01).

[1] N/80 free base was used.

Table XVI.

t.	cc. N/10 NaOH.	k_{base}.	$434.3k_{salt}$
20	10.52	....	....
50	8.80	0.6722	2.59
80	7.38	0.6380	2.57
110	6.26	0.5986	2.51
140	5.29	0.5718	2.40
185	4.25	0.5204	2.38
275	2.60	0.465	2.38

Mean: $434.3\ k_{salt} = 2.47$; $k = 0.00569$.

This gives $k_{ion} = 0.00673$.

The velocity constants for the decomposition of 0.05 molar solution of this salt at 0° (±0.01) in 0.05 and 0.15 molar solutions of hydrochloric acid were also determined. The results are given in Table XVII. Columns 2 and 5 gives the cc. sodium hydroxide used for 25 cc. of the salt solution, *corrected* for the alkali used to neutralize the excess of added acid.

Table XVII.

1. 0.05 molar acid.

t.	cc. N/10 NaOH.	$434.3 \times k_{salt}$.	*t.*	cc. N/10 NaOH.	$434.3 \times k_{salt}$.
0	12.50	....	130	5.71	2.32
10	10.85	....	160	4.86	2.32
40	9.22	2.36	190	4.14	2.33
70	7.80	2.39	291	2.41	2.33
100	6.68	2.34			

Mean: $434.3\ k = 2.34$; $k = 0.00539$.

2. 0.15 molar acid.

t.	cc. N/10 NaOH.	$434.3 \times k_{salt}$.	*t.*	cc. N/10 NaOH.	$434.3 \times k_{salt}$.
0	12.50	....	116	6.72	2.11
21	10.67	....	145	5.78	2.15
55	9.02	2.15	175	4.96	2.16
85	7.83	2.10	205	4.26	2.17

Mean: $434.3\ k = 2.14$; $k = 0.00493$.

In the following table the velocities are referred to the concentrations of the positive imidoester ion only (see Table IV.):

Table XVIII.

$m_{acid.}$	*Est salt.*	$100\alpha_{salt.}$	$434.3k_{salt.}$	$434.3\ k_{salt}/\alpha$
0.00	0.05	84.6	2.47	2.92
0.05	0.106	80.0	2.34	2.93
0.15	0.24	69.0	2.14	3.10

This series shows clearly both the influence of the degree of dissociation of the imidoester salt and also the accelerating "effect" of the acid ions, as developed in Table IV. The series is too short for the determination of an accelerating constant.

7. *The Hydrochloride of Ethyl Imido-m-nitrobenzoate.*

In Table XIX. are given the results of the determinations of the velocity of decomposition constants for a 0.05 molar solution of the hydrochloride alone at 25° (±0.01), and of the 0.05 molar salt in 0.5 and 0.025 molar hydrochloric acid solutions. 25 cc. of the solution were used in each titration, corresponding to 25 cc. N/10 thiosulphate when $t = 0$.

Table XIX.

1. 0.05 molar salt alone.

$t.$	cc. N/10 thio-sulphate.	$434.3 \times k_{salt.}$	$t.$	cc. N/10 thio-sulphate.	$434.3 \times k_{salt.}$
62	4.25	12.4	120	1.19	11.0
120	1.15	11.2	60	4.75	12.0
60	4.73	12.1	120	1.10	11.1

Mean: $434.3\ k_{salt} = 11.67$; $k = 0.027$.

2. 0.05 molar salt in 0.025 molar hydrochloric acid.

$t.$	cc. N/10 thio-sulphate.	$434.3 \times k_{salt.}$	$t.$	cc. N/10 thio-sulphate.	$434.3 \times k_{salt.}$
60	5.08	11.1	60	5.50	11.0
120	1.59	10.0	120	1.37	10.5

Mean: $434.3\ k = 10.64$; $k = 0.0245$.

3. 0.05 molar salt in 0.5 molar hydrochloric acid solution.

$t.$	cc. N/10 thio-sulphate.	$434.3 \times k_{salt.}$	$t.$	cc. N/10 thio-sulphate.	$434.3 \times k_{salt.}$
60	6.39	9.89	60	6.26	10.02
120	1.76	9.60	120	1.78	9.54

Mean: $434.3\ k = 9.76$; $k = 0.0225$.

In Table XX. the columns have the same significance as in Table XVIII.

Table XX.

$m_{acid.}$	*Est salt.*	100α.	$434.3\,k_{salt.}$	$434.3\,k_{salt}/\alpha$.
0.0	0.05	84.6	11.67	13.80
0.025	0.08	82.2	10.64	12.9
0.5	0.80	48.0	9.76	20.3

The series shows the general effect discussed in full for ethyl imidobenzoate, and is too short for detailed analysis. A characteristic fact, however, is that the accelerating "salt effect" of 0.5 mole hydrochloric acid is practically the same in this case $\left(\frac{20.3-13.8}{13.8}=0.47\right)$ as it was found above for ethyl imidobenzoate $\left(\frac{2.36-1.63}{1.63}=0.45\right)$. If the "effect" is indeed due to the increase of the "active mass" of water, we should expect just such a result.[1] This is especially interesting in view of the great difference in the actual velocity constants.

The velocity of decomposition of the salt was also determined at 0° (±0.01) in 0.05 and 0.033 molar solutions.

Table XXI.

1. $V = 20$.

$t.$	cc. N/10 NaOH.	$434.3 \times k_{salt.}$	$t.$	cc. N/10 NaOH.	$434.3 \times k_{salt.}$
0	12.50	...	295	7.79	0.646
55	11.12	...	415	6.50	0.668
175	9.37	0.620	1375	1.66	0.626

Mean: $434.3\ k = 0.639$; $k = 0.00147$; $k_{ion} = 0.00174$.

2. $V = 33$.

$t.$	cc. N/10 NaOH.	$434.3 \times k_{salt.}$	$t.$	cc. N/10 NaOH.	$434.3 \times k_{salt.}$
114	6.83	...	304	5.16	0.641
179	6.18	0.668	1214	1.34	0.643
234	5.71	0.648			

Mean: $434.3\ k = 0.650$; $k = 0.00150$; and $k_{ion} = 0.00171$.

[1] This has been investigated further in this laboratory.—J. S.

In Table XXI*a*. are found the data for the determinations of the hydrolysis constant of this salt at 25° (±0.01).

Table XXIa.

V.	M_v.	Λ_v[1].	100 x.	$10^{-4} K_{hydrolysis}$.
32	94.1	88.13	1.925	8.2
64	100.35	92.8	2.792	7.98
128	107.5	95.4	3.957	7.8
256	112.4	96.9	5.064	9.5
			Mean,	8.4

$k_{base} = 1 \times 10^{-9}$.

8. The Hydrochloride of Ethyl Imido-m-brombenzoate.

In Table XXII. are given the results of the velocity determinations of 0.05 and 0.033 molar solutions of the hydrochloride at 0° (±0.01).

Table XXII.

1. $V = 20$.

t.	cc.N/10 NaOH.	434.3 × k_{salt}.	t.	cc.N/10 NaOH.	434.3 × k_{salt}.
85	11.32	...	1545	5.78	0.213
205	11.15	0.211	1820	5.12	0.209
325	10.52	0.211	2995	2.95	0.207
1325	6.50	0.209			

Mean: 434.3 k = 0.210; k = 0.000483.

2. $V = 30$.

t.	cc.N/10 NaOH.	434.3 × k_{salt}.	t.	cc.N/10 NaOH.	434.3 × k_{salt}.
80	8.03	...	1535	3.93	0.213
200	7.46	0.267	1812	3.41	0.215
320	6.98	0.254	2985	1.88	0.217
1320	4.32	0.217			

Mean: 434.3 k = 0.231; k = 0.000532.

k_{ion} for 0.05 molar solution = 0.000571.
k_{ion} for 0.033 molar solution = 0.000609.

9. The Hydrochloride of Ethyl Imido-β-naphthoate.

The data for the calculation of the velocity of decomposition constants of 0.033 molar solution of the hydrochloride at 25° (±0.01) are given in Table XXIII.

[1] N/80 base was used.

Table XXIII.

$t.$	cc. N/10 NaOH.	$434.3 \times k_{salt.}$	$t.$	cc. N/10 NaOH.	$434.3 \times k_{salt.}$
21	7.93	1.018	201	5.24	1.001
51	7.43	0.970	231	4.91	0.993
82.5	6.92	0.976	261	4.58	0.995
111	6.51	0.965			

Mean: 434.3 $k = 0.988$; $k = 0.00251$.

In Table XXIV. will be found the data for the calculation of the hydrolysis constant at 25° (±0.01).

Table XXIV.

$V.$	$M_v.$	Λ_v[1].	100$x.$	$10^{-5} K_{hydr.}$
32	90.02	87.84	0.878	4.1
64	95.68	91.84	1.25	4.0
128	98.97	95.21	1.23	8.4
256	101.78	96.61	1.687	9.8
				Mean, 6.6

$k_{base} = 7.92 \times 10^{-9}$.

SUMMARY.

1. The nine imidoesters examined are decomposed by water in the presence of acids with a velocity proportionate to the concentration of the salt (positive ions) formed with the acid.

2. The results also contribute evidence that not all the salt present but only its positive ions are decomposed by water. This becomes apparent, not only from the results given in Table IV. (p. 598), taken in conjunction with the "salt effect" summarized in the next paragraph, but also from the following table, in which the velocities referred to the total salt concentrations are compared with the velocities referred to the total positive ion concentrations in all cases where determinations were made with varying concentrations.[2]

Table XXV.

Ester[3]	2.		3.		4.		7.		8.	
k_{salt}[4]	296_{30}	303_{30}	295_{30}	283_{10}	148_{20}	152_{20}	147_{20}	150_{80}	43_{20}	53_{80}
k_{ion}	350	346	349	350	175	174	174	171	57	61

[1] N/100 base was used.

[2] The experiments described here were intended (1899) to test conclusion (1), and they only incidentally contribute to the conclusion reached in (2). This point was investigated *rigorously* in Mr. Schlesinger's later work (1904-5) with more concentrated salt solutions, whose degree of ionization was *measured* (*loc. cit.*).

[3] The numbers in this line refer to the ester used, as numbered in the experimental part.

[4] The numbers used are 10^5 times the true constants. The subindices used give the volume containing a gram molecule of salt.

While the differences are not large, dilute solutions having been used, it is worthy of note that in every case the agreement for k_{ion} for the different solutions is better, and sometimes markedly so, than for k_{salt} (*e. g.*, for ester 3 where the difference in ionization is greatest).

3. The presence of an excess of hydrochloric acid has a twofold effect: it decreases the velocity of the reactions by reducing the degree of ionization of the imidoester salt, thus diminishing the "active mass" of the reacting substance, the positive ester ion; at the same time, an accelerating "salt effect" is decidedly shown, this effect, according to Euler, being probably due, in similar cases, to the increased ionization of the water, *i. e.*, the "active mass" of the second reacting substance is increased, as the other is decreased, by addition of the acid. The acceleration due to this effect was found to be practically the same (45 and 47 per cent) for the same excess of acid (0.5 mole acting on 0.05 molar salt) acting on the salts of two imidoesters whose velocities of decomposition stand in the ratio of about 10: 1. This striking fact tends to confirm the view that the accelerating "salt effect" is, in fact, due, not to any primary action on the salt, but to an effect on the "active mass" of the water involved in the reaction.

4. Table XXVI. summarizes the data obtained in regard to any possible relation between the velocity constants (for 25°) of decomposition according to equation (1) and the hydrolysis constants of equation (2).

Table XXVI.

No.	Ester.	$10^5 k_{ion.}$	$10^{-5} K_{hydrolysis.}$
1.	Ethyl imidobenzoate	377	9.1
2.	Isobutyl imidobenzoate	350	10.4
3.	Isoamyl imidobenzoate	349	14.0
4.	Ethyl imido-*p*-toluylate	175	16.4
5.	Ethyl amino-*o*-toluylate	128	1.9
8.	Ethyl imido-2,6-nitrobenzoate	3200	0.8
9.	Ethyl imido-3-naphthoate	251	6.6

The numbers refer to the number given the esters in the experimental part.

Inspection of the table shows that with two exceptions the velocity constants decrease in the same order in which the strength of the imidoesters as bases (indicated by the rising values of $K_{hydrolysis}$) increases; one of the exceptions, ester No. 5, is the imidoester of *o*-tolunitrile. This nitrile, it will be recalled (p. 603), cannot be converted into an imidoester on account of the stereochemical interference of the methyl group in the ortho position.[1] As in the analogous case of the acid esters, as studied by V. Meyer,[2] the stereochemical interference also delays decomposition of the ester when once formed (from silver salts). We have in this exception, therefore, a further interesting case of parallelism between esters and imidoesters. The other exception is an ester of the naphthalene series. For the strictly comparable esters of the benzene series, we find, as a matter of fact, then, the velocity of decomposition is greatest, the weaker the base is; this points toward the interesting conclusion, based on the real reaction equation which we have established,

$$RC(:\overset{+}{N}H_2)OR + HOH = RCOOR + \overset{+}{N}H_4,$$

that the weaker the base in an analogous series, the less stable is its positive ion, and the more readily does it yield a positive ion (NH_4) of a more easily ionizable base.[3] Whether a widely applicable principle is involved in this, only very extended further investigations can show. My results show that it holds only for the more closely related members of a group,[4] as indicated by the exceptional position of the naphthimido ester, and particularly also by a comparison of the velocity constants (at 0°) for ethyl imidophenylacetate and ethyl imido-*m*-nitrobenzoate.

Table XXVII.

	Ester.	$10^5\, k_{ion.}$	$10^{-5}\, K_{hydrolysis.}$
6.	Ethyl imidophenylacetate	637	3·3
7.	Ethyl imido-*m*-nitrobenzoate	174	0.84

[1] Remsen: THIS JOURNAL, **21**, 281 (1899).

[2] *Loc. cit.*

[3] *Vide* Stieglitz: *Loc. cit.*

[4] A comparative study of the *heats of decomposition* of different groups will be carried out.—J. S.

It is worthy of note, however, that the imidoester of phenylacetic acid, compared with its isomer, *p*-tolylimidoester, and with the closely related esters of benzoic acid, takes its right position in the series.[1]

In conclusion, I desire to express my thanks to Dr. Stieglitz for his help and encouragement in the prosecution of this work.

THE TERPENES OBTAINED FROM INDIVIDUAL SAMPLES OF THE RESIN, MANILA ELEMI.

By A. M. Clover.

During the course of some work with elemi resin, in Manila, it was observed that the oils distilled from different samples of the product, obtained from several dealers, were not the same in composition. While our present knowledge of terpenes does not enable us to determine, even qualitatively, the composition of a mixture of different substances of this class, still certain variations were easily recognized. The low-boiling fractions, which consisted, in all cases, of the simple terpenes only, differed widely in their optical rotation and decidedly, though to a lesser extent, in their boiling point. Phellandrene, limonene and dipentene could be detected in certain cases, and in others could not. The high-boiling portions of the distillate, which were readily separated from the low-boiling terpene fractions, also varied greatly in refractive power and specific gravity. Definite knowledge concerning the origin of the resin was lacking and it was suspected that possibly the product was not derived from a single species of tree. It also seemed possible that changes might have taken place in the resin as a result of long standing.

Later two small, fresh samples, said to have been gathered from single trees, were examined. The low-boiling oil iso-

[1] A comparative study of aliphatic and aromatic acid derivatives and especially of aliphatic acids, RCH_2COOH, $R_2CHCOOH$, R_3COOH, has been planned on the basis of the new lines opened up, especially with the view of obtaining physico-chemical evidence on the formation of $CH_2=CO$ and analogous derivatives as intermediate products. I hope the physico-chemical investigation of this problem will, for a little while yet, be left to us.—J. Stieglitz.

lated from one of these was found to be dextrophellandrene, and that isolated from the other, dextrolimonene, and both were pure so far as the detection of any other terpene was concerned. From botanical material which had been collected from each of the trees, the two were judged to be of the same species.

Most plant products consist of the aggregate obtained from many individuals and I know of no case where chemical differences in the substances produced by individual members of a species have been recognized or suspected. In order to obtain more accurate data upon the subject, I made a trip into the Province of Tayabas, P. I., and in different places collected several samples of the *pili* (Tagalog) resin, from trees differing in size and sex. At the same time leaves of each tree, and also the fruit of those trees bearing it, were preserved. All of the trees appeared to be alike and, from the botanical material, they were all assigned to the species *Canarium luzonicum* by Mr. E. D. Merrill, Botanist to the Bureau of Science of the Philippine Government.

The samples were obtained as fresh as possible, considering the fact that the resin must have remained on the trees for a month or so in order to allow of the production of a fairly large quantity. The different samples were well wrapped in palm leaves and were all worked up within four months after being gathered. The results developed by their examination not only confirmed what had been suspected in regard to variation, but showed that *in the majority of cases, in each individual sample a definite terpene of the limonene series occurred in a pure condition.*

In order to obtain larger quantities of these pure terpenes and to extend the results already obtained, and also with the hope of isolating one or more of the unknown terpenes of this class, another collecting trip was made and 14 more samples were gathered, just as in the previous case. All of these latter were worked up within four months after they were collected. *As a result of the complete examination of 21 samples, it has been possible to isolate the terpenes dextrolimonene, dextrophellandrene, terpinene and terpinolene in pure condition and*

to study the behavior of these substances; to render certain the presence of an unknown terpene in several products; to establish regularities in the occurrence of certain mixtures where the terpene product is not homogeneous; to isolate in pure condition, from single samples, two of the constituents of the high-boiling portion of the oil; and to determine the composition of the mixture which constitutes the high-boiling oil obtained from most samples. The high-boiling oil which occurs in elemi and can be most conveniently and completely removed by distillation *in vacuo* was shown to be a mixture of at least three substances. Here, also, a great variation has been found in the different samples, but no connection appears to exist between the terpene and the corresponding high-boiling oil. No connection can be traced between the age or sex of the tree and the constituents of the oil.

General Data Concerning the Resin and Oil.

From a number of tropical countries products known as elemi find their way into European markets. The species from which most of these varieties are derived is unknown, but there is little doubt that they are all to be referred to the general order of *Burseraceae.* A. Tschirch and J. Cremer[1] have recently arrived at the definite conclusion that Manila elemi is derived from *Canarium commune* L. Their conclusion is the result of an examination of samples of Manila elemi and resin obtained by one of the authors in India from the species *Canarium commune,* and is based upon a comparison of the general properties of the two products as well as of the crystalline substances isolated therefrom. So far as their work went they were unable to note any differences between the two products.

The tree *Canarium luzonicum* is quite widely distributed in the Philippine Islands and is known by the Tagalogs as *pili.* There are two closely related species designated as *pili. Canarium luzonicum* bears a small nut, while the other, which has been identified by Mr. Merrill as *Canarium pachyphyllum,* bears a much larger nut, produces resin in only very

[1] Arch. d. Phar., **240**, 313 (1902).

small amounts, and is never used by the natives as a source of the latter.

In the Philippines the resin is commonly known by the Spanish term *brea*, which is applied by the natives indiscriminately to all similar products. As ordinarily gathered for commerce, the resin is soft, sticky and opaque and has a slightly yellow color and an agreeable odor. If not frequently removed from the tree it hardens and loses a portion of its oil through volatilization and oxidation. The fresh resin contains nearly five per cent of water and about thirty per cent of volatile oil. The latter is composed of about equal parts of a low-boiling portion, consisting of terpenes, and of a high-boiling portion, containing oxygen compounds.

Elemi oil, usually obtained by steam distillation of the resin, has long been known to chemists. Gildemeister and Hoffmann[1] state that at present the commercial product is prepared from Manila elemi exclusively, although in most cases where the oil has been used in chemical investigations there seems to be much doubt as to its origin. The oil was first studied by Stenhouse,[2] and some years later Deville[3] obtained from it dipentene hydrochloride. Wallach[4] detected phellandrene and dipentene in the oil and has used it as a source of these substances. He also noted the presence of high-boiling oxygen compounds. Schimmel and Co., in their semiannual report of October, 1896, publish some observations concerning the high-boiling portion of the oil. Tschirsch and Cremer[5] have distilled Manila elemi, as well as other varieties, with steam and obtained oils, but the very meagre data which they give do not enable one to decide what differences, if any, exist in the oils.

Distillation of Resin and Purification of Oils.

Owing to the fact that the resin becomes more and more viscous as the volatile oil is removed, the distillation with

[1] **Die aetherischen Oele, Berlin (1899).**
[2] **Ann. Chem. (Liebig), 35, 304 (1840).**
[3] *Ibid.*, **71,** 352 (1849).
[4] *Ibid.*, **246,** 233 (1888); **253,** 102 (1889).
[5] *Loc. cit.*

steam is slow and unsatisfactory. It was desired to remove all the oil possible and at as low a temperature as possible, in order to prevent any change taking place in it. For this purpose it was found much better to distil in a vacuum. It was also found that the high-boiling oil could be almost completely removed from the resin at a pressure varying from 8 to 15 mm., with practically no decomposition of the latter. To introduce the resin into the distilling flask, it was first placed in a beaker and immersed in an oil bath which was kept at a temperature of from 100° to 125°, depending on the ease with which the resin became fluid. The latter was then poured into the flask and the terpene oil distilled over *in vacuo*, the pressure being gradually decreased to 10 or 15 mm. as the water in the resin passed over; the oil bath was kept between 125° and 150°. The distillation was always made as quickly as possible and in no case was purified terpene oil derived from a product which had been heated higher than 150°. Frequently a second distillate was then taken by heating to 200°, at which temperature practically all of the terpene but only a portion of the high-boiling oil may be removed. If the resin is quite fresh, most of the heavy oil will have passed over before the oil bath reaches 230°, but with an old product it is difficult to maintain a high vacuum, so that the oil bath must be heated to 250°. At this temperature, with fresh material, there is very little, if any, decomposition of the resin, but with old samples it is possible to remove only a small portion of the high-boiling oil because of the increasing difficulty of maintaining a vacuum as the temperature is raised beyond 200°. In several instances, the purified, high-boiling oils derived from fresh resin at 200° were found to be identical with those obtained from the same samples when, in some cases, the temperature was raised as high as 250°; so that it is quite certain that no changes have been brought about in these oils by the high temperature.

Sample I. was collected in July near Unisan, Tayabas Province, Luzon, from a relatively young tree about 40 feet in height, having a diameter of about 2 feet near the base. There was no fruit on the tree and its owner said it never had borne

any. The resin was drier than most of the samples and yielded only about seventeen per cent of oil.

The first distillate (I,A) was taken at 140°, the second up to 210° (I,B), and the third up to 250° (I,C).

I,A was redistilled twice at 54 mm.; it passed over completely, the second time, from 93° to 94° (I,A, purified). Its optical rotation was $\alpha_D^{30} = +99°.6$.[1] The oil gave no test for phellandrene. It was found that on the addition of even only 1 per cent of an oil known to be nearly pure phellandrene, it responded plainly to the test when the solution was kept very cold. In the proportion of 1 to 200 no test could be obtained. With bromine in acetic acid, limonone tetrabromide was obtained. This melted at 104°–105° after the second crystallization from alcohol. The oil, treated with hydrochloric acid gas in glacial acetic acid, gave a good yield of dipentene dihydrochloride, which, after recrystallization from alcohol, melted at 49°–50°. I,A, purified, gave a granular nitrosylchloride when treated according to the method of Wallach. The odor of the oil was plainly that of commercial carvene. When heated with metallic sodium it was very little affected, and after having been distilled from the metal it was found to pass over completely at ordinary pressure from 176°.5 to 177°.5. It appears to be pure dextrolimonene.

Sample II. was collected near Atimonan, Tayabas, from a tree having a diameter of about 3 feet near the base and laden with unripe nuts. The sample was softer than the previous one and yielded 25 per cent of oil.

The first distillate was taken at 125° (II,A), the second at 210° (II,B), and the third at 250° (II,C).

II,A was decanted from a small amount of water which collected with it. It was distilled twice at 36.5 mm., passing over the second time almost completely between 82°.5 and 83°.5; three-fourths of it distilled at almost a constant temperature, or at most within 0°.25 (II,A, purified). $\alpha_D^{30} = +100°$. The product, so far as could be determined, was identical with that obtained from *Sample I.*

[1] This form of expression will be used to express the rotation in a ten cm. tube at the temperature indicated.

Sample III., which was quite soft, was obtained from a young tree, smaller than that from which *Sample I.* was taken, and standing very close to the latter tree. It was first distilled at 125° for the terpene oil (III,A) and then at 210° (III,B). In all, 186 grams of distillate were obtained from 900 grams of resin. A further distillation was not made.

III,A, on the third distillation at 47 mm., passed over completely from 89° to 90°. $\alpha_D^{30} = +100°.7$. The purified oil had the same odor, boiling point and optical rotation as the two previous terpene products.

Sample IV. was collected near Unisan, Tayabas, from a good-sized tree, nearly 3 feet in diameter near the base. The tree, which bore no fruit, contained 8 to 10 pounds of soft resin.

One thousand and eighty grams of the sample were distilled, first at 125° (IV,A), then at 210° (IV,B) and finally at 250° (IV,C). The total amount of terpene oil obtained from this sample was 152 grams, or 14 per cent, and of high-boiling oil, 145 grams, or 13.4 per cent.

IV,A was redistilled twice at 65.5 mm., and on the second distillation it passed over completely from 95°.5 to 97°.5 (IV,A, purified). It was almost optically inactive ($\alpha_D^{30} = +4°$). It gave no test for phellandrene. In a check experiment in which a very small proportion of phellandrene was added to the oil, this was easily detected. No crystalline hydrochloride could be obtained on treatment with hydrochloric acid gas in cold, glacial acetic acid, nor could a crystalline bromide be separated on saturation with bromine, either in acetic acid or in a mixture of amyl alcohol and ether. No solid nitrosylchloride could be obtained. A good quantity of terpinene nitrite was obtained by using the method recommended by Wallach, the crystals appearing in a short time. When recrystallized from alcohol, this substance melted at 155°, softening a little below that temperature. The oil was distilled from metallic sodium, after which it boiled completely from 174° to 176°. It stood nearly a year in a partially filled glass-stoppered bottle; it was then redistilled with steam, separated from water, and dried over solid caus-

tic potash. Boiling point, 174° to 175°.5. Sp. gr. $\frac{30}{4}$ = 0.8358. $\alpha_D^{30} = +4°.3$. $n_D^{30} = 1.4756$. The product still gave a good yield of terpinene nitrite and in all other respects it behaved as it had one year previously. It appears to be almost pure terpinene. In physical properties it does not differ much from limonene except in refractive power (see page 631). Terpinene has been detected in only two of the natural essential oils. It has also been shown to be present in several products resulting from chemical operations in the laboratory. In general, those fractions boiling at about 180° appear to have given the best yield of the nitrite.

IV,B was distilled under reduced pressure and the low-boiling portion was refractioned. On the third distillation it passed over completely, within a range of 2°.5 or 3°, and was evidently not so pure a product as that obtained from IV,A, although it gave a good yield of terpinene nitrite. It appears that in this case, as well as with the samples containing phellandrene, there is some alteration in the terpene when it is removed from the resin at higher temperatures.

Sample V., which was moderately soft, was obtained from a tree standing close to that from which *Sample II.* was taken. The tree was laden with unripe nuts.

The resin was distilled, first at 125° (V,A), then at 210° (V,B) and finally at 250° (V,C). The total terpene oil amounted to 9.7 per cent and the high-boiling oil to 15.8 per cent.

V,A, on the second distillation at 43.5 mm., passed over almost completely from 82°.7 to 84° (V,A, purified). Its odor was very pleasant and markedly different from that of any of the terpene products previously obtained. $\alpha_D^{30} = +122°.6$. It yielded a very heavy precipitate of phellandrene nitrite. Neither a solid bromide nor a nitrosylchloride could be obtained by the methods ordinarily used. The product appears to be almost pure phellandrene. Its boiling point is 3° or 4° below that of the limonene oils and about 2° below that of the terpinene oil. On standing in a partly filled glass-stoppered bottle, a small amount of good-sized, colorless, prismatic crystals appeared about the walls of the bottle.

Sample VI. was obtained near Atimonan, Tayabas. The

tree was an unusually large one, being 5 or 6 feet in diameter near the base. A large quantity of soft resin had accumulated from a number of cuts. The tree bore no nuts and a native familiar with it declared that it had never produced any.

The first distillate (VI,A) was taken at 125°, and the second up to 225° (VI,B). The two amounted to 25 per cent of the resin.

VI,A passed over completely from 93° to 94° at 55 mm. on the second distillation (VI,A, purified). It had the same characteristic odor as the product obtained from the previous samples of limonene which had been isolated and its boiling point is also the same. $\alpha_D^{30} = +99°.9$. In rotation, its agreement is seen to be remarkable. Pure limonene tetrabromide was obtained from it and it was also tested thoroughly, just as the oils from *Samples I.* and *II.*, and it showed exactly the same behavior. By comparing the terpene oils obtained from *Samples I.*, *II.*, *III.* and *VI.*, especially as to rotation, it appears that when dextrolimonene occurs in the resin from a single tree it is present in pure condition.

Sample VII. was obtained near Atimonan, Tayabas, from a tree about 2 feet in diameter, laden with unripe nuts. The sample was a little hardened, but only on the outside.

Nine hundred and sixty grams were distilled, first at 125°, yielding 57 grams of distillate, excluding 3 or 4 grams of water (VII,A). A second portion, 128 grams, was taken to 210° (VII,B), and a third, 73 grams, to 250° (VII,C). The total distillate, 258 grams, consisted of about equal parts of terpene oil and heavy oil, or 13.4 per cent of each.

VII,A, on the third distillation at 39 mm., passed over from 76°.5 to 79° (VII,A, purified). $\alpha_D^{30} = +114°.7$. The product had the odor of phellandrene, but it also possessed another peculiar odor not noticeable in any of the other terpene products. Its initial boiling point is a few degress lower than that of the sample of presumably pure phellandrene already isolated. The oil gave a precipitate of phellandrene nitrite in good quantity, but many attempts to isolate any other crystalline derivative from it by any of the methods ordinarily employed were unsuccessful. The product was

then distilled at ordinary pressure and two fractions of equal size were taken—(1) from 167°.5 to 169°; (2) from 169° to 172°. The first fraction showed a rotation of +110°.1 and the second +113°.1. The first fraction was tested in a number of ways in the hope of isolating a crystalline substance other than phellandrene nitrite, but with negative results. On again distilling, its initial boiling point was lowered only about 0°.5. Both fractions deposited crystals on standing.

The work with the following samples was carried out in essentially the same manner as that already detailed. It was found that it was not necessary to use great precaution as to temperature in removing limonene from the resin; therefore, when a sample was found to contain dextrolimonene, the terpene was removed as completely as possible by heating the resin to 150° or 160°. Phellandrene suffers a considerable change at a temperature near its boiling point, and it was thought that terpinene would likewise suffer alteration at a higher temperature, especially when it was in contact with the resin. However, it was desirable to remove all of the terpene possible, so that the purified product could be used for further work. In those samples not containing dextrolimonene, the distillation was carried as far as possible at 125° and then the oil bath was heated gradually to 150° and the distillation made as quickly as it could be done. The entire distillate was taken in only two portions, the high-boiling part being seldom taken beyond a temperature of 235°. The products will be designated as A, first distillate, and B, second distillate. In order to obtain the correct data for the physical properties of the terpene oils, they were, unless otherwise stated, first shaken with a dilute solution of potassium hydroxide which freed them from an unpleasant odor often noticed, and then distilled twice *in vacuo*, allowed to stand overnight with solid potassium hydroxide, and then carefully redistilled, the first 2 or 3 cc. of the distillate being discarded. In a few samples, the high-boiling oil was disregarded entirely. The following samples were all obtained within a radius of a mile or two near the town of Gumaca, Tayabas, during the month of June.

Sample VIII. was taken from a tree a little over 2 feet in diameter. The tree bore no fruit. The resin had evidently collected for some time, there being a large amount of it, yellowish and somewhat incrusted, on the tree. The purified terpene oil boiled completely from 95°.3 to 96°.5, at a pressure of 60.5 mm., and at ordinary pressure from 176° to 176.°7. $\alpha_D^{30} = +100°.8$. It is evidently pure limonene.

Sample IX. was obtained from a tree, laden with nuts, of about the same size as that from which *Sample VIII.* was taken and standing close to the latter tree. The sample was a large one and somewhat dried out. The purified terpene oil boiled from 176°.5 to 177°.5. $\alpha_D^{30} = +100°.3$. It is evidently pure dextrolimonene, but the boiling point is slightly higher than that of the last sample.

Sample X. was taken from a medium-sized tree bearing fruit. The resin was fresh and soft. The terpene oil, after the usual purification, distilled completely from 89°.5 to 94°.5 at 65 mm., so that, therefore, the distillation began about 5° below the boiling point of phellandrene. $\alpha_D^{30} = +69°.3$. It gave a heavy precipitate of phellandrene nitrite. It was redistilled at ordinary pressure and the distillate divided into two equal portions: (1) 166°.5 to 168°.5; (2) 168°.5 to 171°.5. The first fraction showed sp. gr. $\frac{30}{4} = 0.8356$; $\alpha_D^{30} = +70°.4$; $n_D^{30} = 1.4663$; while the second gave sp. gr. $\frac{30}{4} = 0.8374$; $\alpha_D^{30} = +64°.6$; $n_D^{30} = 1.4680$. The first fraction was redistilled and there was very little lowering of the initial boiling point. The phellandrene nitrite obtained from the oil was recrystallized twice from hot acetic ester and it then melted at 114° to 115°. In its odor and boiling point this oil is very much like that obtained from *Sample VII.*; however, it seems to contain much more of the lower-boiling terpene. It appears from the data just given that this terpene has a considerably lower refractive power and specific gravity than phellandrene. As with the oil of *Sample VII.*, it was not found possible to obtain any solid derivative except phellandrene nitrite.

Sample XI. was small in amount, and to obtain enough terpene oil to work with, the latter was completely removed

at a temperature of 200°. The oil was not purified *in vacuo* but was redistilled twice at ordinary pressure, passing over the second time mostly from 173° to 178°; $\alpha_D^{30} = -50°.7$. This is the only case in which a levorotatory oil has been obtained from a sample of elemi. The oil gave a precipitate of phellandrene nitrite, but the yield was not large. In cold, glacial acetic acid a tetrabromide was separated, but a much better yield was obtained in amyl alcohol and ether. When recrystallized twice from alcohol, it showed a melting point of 104° to 105°. The tetrabromide of levolimonene in chloroform at 9° and at a concentration of 12.85 per cent gives $[\alpha]_D = -73.45$, as determined by Wallach and Conrady.[1] The amount of pure bromide at hand was not large enough for an accurate estimation, but it was found to be levorotatory and to about the degree just mentioned. A small portion of it was carefully weighed out and mixed with exactly the same amount of pure dextrolimonene tetrabromide. The mixture was dissolved in a small amount of acetic ester, and alcohol was then added. On cooling, pure dipentene tetrabromide, melting at 124°, crystallized out. The oil, therefore, contains levolimonene and phellandrene, the latter being probably dextrorotatory. That the levolimonene was not formed by the action of heat upon the phellandrene will be seen from experiments given under phellandrene.

Sample XII. was taken from a medium-sized tree which bore no fruit. The resin was quite soft. The purified terpene oil obtained from this sample showed a boiling point of 176° to 176°.7 at ordinary pressure. $\alpha_D^{30} = +100°.3$. It is evidently pure dextrolimonene.

Sample XIII. was a large accumulation, somewhat incrusted, taken from a medium-sized tree with no fruit. The purified terpene oil was found to be pure dextrolimonene. Boiling point, 176°.5 to 177°.5; $\alpha_D^{30} = +100°.1$.

Sample XIV. was taken from a medium-sized tree bearing fruit. The resin was moderately soft. The purified terpene oil boiled from 91°.5 to 93° at 60 mm. Sp. gr. $\frac{30}{4} = 0.8322$; $\alpha_D^{30} = +105°.1$; $n_D^{30} = 1.4694$. The oil gave a heavy pre-

[1] Ann. Chem. (Liebig), **252**, 145 (1889).

cipitate of phellandrene nitrite. To judge from the boiling point, the oil appears to be nearly pure phellandrene, although the rotation is considerably lower than that of the phellandrene from *Sample V.*

Sample XV. was obtained from a very large tree, bearing no fruit. It was quite soft. The purified terpene oil boiled from 88° to 91° at 60 mm. Sp. gr. $\frac{30°}{4}$ = 0.8336; $\alpha_D^{30°}$ = +112°.7; $n_D^{30°}$ = 1.4678. The initial boiling point was a little below that of phellandrene and the product was evidently a mixture. It gave a heavy precipitate of phellandrene nitrite. The oil redistilled at ordinary pressure from 169°.3 to 172°. The distillate was divided into two fractions, which showed practically the same rotation, a trifle lower than the original. No other crystalline derivative could be obtained from the oil. The odor is at once suggestive of the oils from *Samples VII.* and *X.*, which this oil resembles in most respects. During the purification, crystals were noted in the small residue contained in the distilling flask. Crystals also separated from the heavy oil which had been redistilled once and allowed to stand.

Sample XVI. was obtained from a good-sized tree about 3.5 feet in diameter near the base and bearing no fruit. The resin was fresh and soft. The purified terpene oil distilled completely from 89° to 90°.8 at 56.5 mm., most of it going over at almost a constant temperature. $\alpha_D^{30°}$ = +129°.8; in a 5 cm. tube the rotation was just one-half as great. The oil had the characteristic odor of phellandrene and gave a heavy precipitate of the nitrite. A portion distilled completely at ordinary pressure from 172° to 173°.5. The product has the highest rotation of any sample of phellandrene obtained.

Sample XVII.—The purified terpene oil distilled almost completely from 86° to 87°.5 at 48.5 mm., a little higher, therefore, than the temperature at which phellandrene should distil. It contained much phellandrene but the rotation, as well as the boiling point, indicated that some other substance was present. $\alpha_D^{30°}$ = +73°.5; $n_D^{30°}$ = 1.4693. A portion of it distilled from 173° to 174°.5 at ordinary pressure. No

crystalline bromide could be obtained in acetic acid, nor in ether and amyl alcohol. No limonene could be detected by tests with ethyl nitrite in acetic acid or in ligroin. In preparing phellandrene nitrite, no crystals of terpinene nitrite appeared in the mother liquor on standing. The crude phellandrene nitrite was dissolved in a small amount of chloroform, filtered and precipitated with ether. It then melted at 114° to 117°. On recrystallizing from acetic ester without warming, it melted at 119°.5 to 121°. On again recrystallizing it melted at 120° to 121°. The crude nitrite obtained constituted about 50 per cent of the weight of the original oil. The rotation of the nitrite melting at 119°.5 to 121° was approximately that found by Wallach for pure α-phellandrene α-nitrite obtained from several sources, so that it appears that the low rotation of this sample of phellandrene and the variation observed in the rotation of the other samples obtained are not to be explained by assuming the presence of varying amounts of levophellandrene. It will be brought out later that the second substance in this oil is levolimonene.

Sample XVIII.—The purified terpene oil distilled completely from 88°.7 to 90°.4 at 54.5 mm. pressure. It was found to be phellandrene and, judging from the boiling point, was almost, if not quite, pure. The rotation, however, is somewhat lower than that of some of the phellandrene oils ($\alpha_D^{30} = +113°.5$). After standing for two months the sample contained a small quantity of the familiar crystals.

Sample XIX. gave a purified terpene oil boiling from 90° to 91° at 50 mm. pressure. $\alpha_D^{30} = +98°$; $n_D^{30} = 1.4680$. It is evidently practically pure limonene, although the rotation is a little lower than usual. It was found impossible to isolate from the high-boiling oil of this sample any considerable portion which would show a narrow range in boiling point.

Sample XX.—The purified terpene oil from this sample distilled completely from 81.7° to 83° at 35.5 mm. $\alpha_D^{30} = +97°$. The substance appeared to be practically pure limonene, although the rotation is lower than that of any other sample isolated. It gave no test for phellandrene.

Sample XXI. proved to be especially interesting. It was small in amount and was a fresh, soft resin when collected, although nearly four months elapsed before it was distilled. The terpene oil passed over on the second distillation almost completely within 1°, the boiling point lying between that of phellandrene and limonene. Its rotation was +4°. Because of its rotation and boiling point, it was at first supposed to be terpinene, but no test for terpinene could be obtained. The oil contained no phellandrene, according to notes made at the time it was distilled. There can be no doubt on this point, as the phellandrene nitrite would certainly have been noted in the test for terpinene, the tests always being made in essentially the same manner. On long standing, even after having been inoculated with a crystal of terpinene nitrite, no separation of this substance occurred. On the same day that the test for terpinene was made and when it was found that the terpinene nitrite was not being formed, the oil was treated with bromine in cold acetic acid and a crystalline bromide obtained. This was recrystallized from acetic ester. The crystals did not appear to be those of dipentene tetrabromide, as they melted at about 117°, with darkening and effervescence. The substance was recrystallized from alcohol, in which it appeared to be more soluble than dipentene tetrabromide. The crystals were lustrous plates and melted at 116°, with darkening and effervescence. It was noted at the time that these crystals were entirely different from those of dipentene tetrabromide, with which I was very familiar and which I rather expected to obtain when the test was made. The substance was certainly the tetrabromide of terpinolene, discovered by Wallach[1] in the product formed by the action of sulphuric acid upon American turpentine oil. He also obtained it from the oils resulting from the action of sulphuric acid upon terpine hydrate, terpineol and cineol. He gives 185° to 190° as the boiling point of the fraction yielding the bromide in the first case noted. Baeyer[2] also studied the substance and found that the bromide was best prepared from

[1] Ann. Chem. (Liebig), **230**, 262 (1885); **239**, 23 (1887).
[2] Ber. d. chem. Ges., **27**, 447 (1894).

the oil which resulted from the action of a boiling solution of oxalic acid upon terpineol. By reducing the tetrabromide with zinc dust in cold acetic acid, Baeyer obtained a product which boiled from 183° to 185° and which gave a good yield of the tetrabromide. He found the terpinolene to be rapidly changed by the action of heat.

The oil from the sample, as described above, was, as usual, shaken out with a dilute solution of caustic potash and then dried over solid caustic potash. It was redistilled on the next day, and at 37 mm. its boiling point was practically constant, 80° to 81°. The physical constants of the oil were now as follows: Sp. gr. $\frac{30}{4}$ = 0.8360; α_D^{30} = +1°.7; n_D^{30} = 1.4701; boiling point, 173°.5 to 175°.

Up to this time only one day had elapsed since the removal of the oil from the resin. The alteration in its rotation between the second and third distillations was thought to be unusual and, with the idea of accelerating any change which was possibly taking place in the oil, a portion of it was heated for 3 hours in a tightly-stoppered distilling bulb, immersed in an oil bath at 200°. The product was then distilled. The range in boiling point appeared to be greater than before heating. The amount of polymerization was very small. *The distillate showed a rotation of* —7°.5, and was found to give a precipitate of *phellandrene* nitrite, although the amount obtained was not large. After the usual treatment of the crude product, namely, dissolving it in chloroform and precipitating with ether, it was recrystallized from acetic ester without warming and found to melt at 119° to 120°. The quantity was small, but a reading made in an approximately 1 per cent acetic ester solution showed it to be decidedly levorotatory.

Four or five days later an attempt was made to prepare more of the terpinolene tetrabromide from the purified oil. The tetrabromide obtained in acetic acid was recrystallized from acetic ester and now melted at about 120°. It appeared more like dipentene tetrabromide than like the derivative of terpinolene, and on recrystallization melted at 125°. The experiment was carefully repeated twice; the bromine, dis-

solved in an equal volume of glacial acetic acid and well cooled, was carefully added to an equally well cooled solution of the oil in 1.5 volumes of glacial acetic acid. The crude bromide, when recrystallized from acetic ester, melted from 118° to 120° with darkening, but in appearance and solubility it resembled dipentene tetrabromide. On recrystallizing again, it melted at 123° to 124°. The purified bromide was unquestionably that of dipentene, although the crude product appears to have been a mixture, for after the first recrystallization it was still impure.

At this point it was found that the purified oil gave a decided test for phellandrene. The rotation of the oil was also found to have changed from +1°.7 to —1°.6. *After standing for five or six days longer, the oil gave a rotation of —9°.8 and one month after this, of —34°.5, thus demonstrating that a rapid change was taking place spontaneously.* Three weeks later, the oil, which had stood in a cork-stoppered, partly filled flask, was distilled with steam. A small proportion of viscous, nonvolatile matter remained, probably the result of oxidation of the oil on standing. The distillate was separated from water, and without further drying gave α_D^{30} = —38°. Judging from this value, in comparison with that obtained three weeks previously, it was evident that the change taking place had about reached completion. In amyl alcohol and ether the oil now yielded a very good quantity of a crystalline bromide which was recrystallized from a mixture of acetic ester and alcohol. The crystals melted at 122° to 124°. 0.24 gram of the substance dissolved in about 8 cc. of acetic ester and placed in a 10 cm. tube showed no appreciable rotation, so that the product apparently contained very little, if any, limonene tetrabromide. Certainly, the rotation of the oil cannot be accounted for by the presence of levolimonene. A good quantity of the bromide was also obtained in acetic acid. After crystallizing once from a mixture of acetic ester and alcohol, it melted at 120° to 123°; on recrystallizing from acetic ester its melting point was 125°. The product melting at 120° to 123° remained perfectly colorless on fusion, thus differing markedly from that

obtained from the oil after four or five days' standing. An attempt was now made to prepare phellandrene nitrite again from the oil and to determine its rotation. Although the presence of phellandrene in the oil was readily shown, it was found impossible to isolate the nitrite in the presence of so much dipentene, the final product being a small amount of viscous matter adhering to the sides of the flask. This result is, of course, quite different from that obtained two months previously.

There appears to be no doubt that the oil, when first isolated, was nearly pure terpinolene; that this terpinolene changed completely, on standing, into dipentene, a small amount of dextrophellandrene and an unknown levorotatory terpene. The boiling point of this terpinolene is considerably lower than that obtained by Baeyer for the product formed on reducing the tetrabromide. The present case is the only one in which the presence of terpinolene has ever been noted in a natural product.

Limonene.

Limonene occurs generally in the dextrorotatory form as the chief component of a number of the most important essential oils of commerce. From some of these it has been obtained in a fair degree of purity by fractional distillation, but the physical properties of the substance, as given in the literature, vary somewhat, depending upon the degree of purity with which it is possible to isolate it from the other constituents of those oils by the process mentioned. From caraway oil, Schimmel & Co.[1] have isolated dextrolimonene, which showed a rotation of $[\alpha]_D = +123°.6$, while Kremers[2] obtained $[\alpha]_D^{20} = +120°.46$ for the carefully fractionated portion of commercial carvene boiling at 174°.5 to 175°, and presumably from the same source. For the levolimonene of pine-needle oil, Wallach found $[\alpha]_D = -106°$. Godlewsky and Robhanowitsch,[3] for the purpose of obtaining accurate data as to its physical constants, prepared what appears to

[1] Gildemeister und Hoffmann: Die aetherischen Oele, 1899, p. 172.
[2] This Journal, 17, 694 (1895).
[3] Centrabl., 1899, I., 1241.

be almost, if not quite, pure limonene by reduction of the pure tetrabromide. Their product, which is described as boiling at constant temperature, showed: sp. gr. = 0.8425; $[\alpha]_D^{20} = +125°.6$; boiling point, 177°.5 at 759 mm. Considering the small variation which I have found in the optical activity of the many constant-boiling samples of dextrolimonene obtained from different samples of elemi, this property appears to serve well as a check upon the purity of the limonene.

The following table of physical constants for dextrolimonene is taken from some of the samples which have a rotation close to the average:

Purified product.	Boiling point, complete.	α_D^{30} +	n_D^{30}	Sp. gr. $\frac{30}{4}$	Boiling point at reduced pressure.	mm.
VIII,A	176.0–176.7	100.8	1.4679	0.8353	95.3–96.5,	60.5
XII,A	176.0–176.7	100.3	1.4682	0.8350		
XIII,A	176.5–177.5	100.1	1.4683	0.8364		
IX,A	176.5–177.5	100.3	1.4680	0.8371[1]		
VI,A	176.0–176.7	99.9	....	....	93–94	55
II,A	176.0–177.0	100.0	....	....	82.5–83.5,	36.5

Product VIII,A, purified, showed: $n_D^{25} = 1.4705$ and $n_D^{20} = 1.4728$. An average difference of 0.0071 was found between specific gravity $(\frac{30}{4})$ and specific gravity $(\frac{20}{4})$ for three samples. The molecular refraction of limonene at 20° may, therefore, be calculated.

The value of the rotation given corresponds very closely to that noted by Kremers. The latter states that the rotatory power of limonene changes considerably on standing, giving, as an instance, a sample whose rotation had changed from +121°.3 to +103°.23. He also notes a corresponding increase in the specific gravity. I have found that a sample of pure limonene, sealed up in a flask which was nearly full, suffered no noticeable change after standing four months, but several samples of pure limonene which were kept in glass-stoppered bottles were found to decrease gradually in rotatory

[1] The high number probably has its cause in the age of the resin; the product was notably more difficult to purify than any of the others. Unfortunately, several of the samples of pure limonene were used up before their physical constants had been accurately determined.

power; the same is true of phellandrene. The change is undoubtedly caused by oxidation of the terpene. One sample of limonene which originally had a rotation of $+100°.6$ stood for about a year in a partly filled, glass-stoppered bottle. It was then redistilled with steam. A considerable amount of nonvolatile matter remained behind and the distillate had taken on an odor resembling that of menthol. The oil was redistilled *in vacuo* and then showed a rotation of $+100°.2$. It distilled completely from $176°.5$ to $177°.5$.

In this connection the behavior of limonene at elevated temperatures was also studied. Wallach[1] states that hesperidene (dextrolimonene obtained from oil of orange) is changed into dipentene by "*mehrstündiges*" heating at 250° to 270°, and a similar statement, probably derived from this source, appears in many of the books dealing with this subject.

(1) Twenty-five grams of pure limonene ($\alpha_D = 100°.7$) were heated in a sealed tube at 275° to 290° for five hours. The product was then distilled with steam. A small amount of nonvolatile matter, about 5 per cent of the original, remained behind. The polymerized product is only slightly soluble in alcohol. The distillate, after having been dried over solid potassium hydroxide, showed exactly the same boiling point as the original. Its rotation was $+99°.8$ and its refractive index was practically unchanged. A tetrabromide, prepared in acetic acid, after being recrystallized once from acetic ester, melted at 104°–105°, this being the melting point of pure limonene tetrabromide.

(2) The limonene obtained from the last experiment was heated, together with 2 or 3 drops of water, in a sealed tube at 290° for ten hours, the temperature rising to 360° for a short time. On examining the contents of the tube the water still appeared and the product was colorless. After distilling with steam, about 10 per cent was found to have been polymerized. The distillate, when dried, showed the same boiling point as before. The rotation had decreased a little: $\alpha_D^{30} = +97°$.

(3) Twenty grams of pure limonene, together with 2 drops

[1] Ann. Chem. (Liebig), **227**, 289 (1885).

of water, were heated in a sealed tube at 200° for ten hours. The amount of polymerization was small. The boiling point was unchanged, as well as the refractive index, although the rotation had decreased 0°.5.

(4) Twenty grams of pure limonene, together wth 1 gram of benzoic acid, were heated in a sealed tube at 250° for seven hours. The product was extracted with a small amount of potassium hydroxide solution and all of the benzoic acid was recovered. It was then distilled with steam, only a small amount of residue remaining. After drying, the oil was redistilled and the boiling point found to be practically unaltered, although the rotation had decreased from +100°.1 to +98°.

(5) Twenty grams of practically pure limonene, together with 1 gram of acetone, were heated at 300° for six hours. The product was colorless. There was considerable polymerization. The boiling point of the oil was unchanged but the rotation had decreased from +98° to +96°.5.

(6) About 20 grams of pure limonene, with 2 grams aniline, were heated at 280° for seven hours. The product was extracted with very cold, dilute hydrochloric acid and distilled with steam. It then distilled completely from 176° to 177°. The rotation had decreased from +100°.2 to 99°.4.

(7) A few grams more of the pure substance were added to the limonene obtained from the last experiment and it was heated at 380° for six hours. The product was colorless. Approximately 15 per cent of the total had been polymerized. The boiling point of the distillate was unchanged, although the rotation had decreased to +93°.

It will be seen from the above experiments that if dipentene is formed from dextrolimonene at elevated temperatures the change is an extremely slow one. Even at 380° it would take many hours for its formation in sufficient amount to be detected. Moreover, it does not follow that a decrease in the rotation implies the formation of dipentene, although, from the unchanged boiling point, this seems probable. It will also be noted that the degree of polymerization is more than double that of inversion. From these experiments limonene

is seen to be a very stable substance and almost indifferent to the influence of foreign reagents, even with respect to its optical activity. It may be distilled repeatedly at ordinary pressure without suffering alteration. It was found that after heating for eight hours in a tightly-stoppered distilling bulb in an oil bath at a temperature of 180° to 220° the distillate was identical in all respects with the original, except that its rotation had decreased by about 0°.2.

α-Phellandrene.

Reliable data concerning the terpene itself are wholly lacking. The physical properties recorded vary somewhat, but, with the exception of the rotation, do not differ greatly from those which I have found for pure phellandrene. Although phellandrene may be the predominant terpene in many of the fractioned products described in the literature, it must be remembered that the values of the physical constants of most of the terpenes of this series are very nearly equal to each other and as it appears often to be true that only terpenes of a certain class are to be found in the oil obtained from any one species, an admixture of a considerable percentage of one would have only a slight effect on the values of another. The optical rotation (α_D) of well-fractioned phellandrene products is seldom given as being higher than ±60°. Although phellandrene appears to be converted completely into the nitrite, it was found almost impossible to dry the filtered and well washed product so as to weigh it accurately. This difficulty is caused by the tendency of the crude substance to become slightly resinous. In solvents it undergoes rapid decomposition.

In nearly all of the terpene oils obtained in this work which were found to contain phellandrene, the latter was examined and found to be α-phellandrene, determined by isolating the α-nitrite described by both Schreiner[1] and Wallach.[2] The method usually employed was to dissolve the crude product, dried as well as possible by pressure between filter paper, in a very small amount of chloroform, then to filter to remove the

[1] Centrabl., **1901**, II., 544.
[2] Ann. Chem. (Liebig), **324**, 269 (1902); **336**, 9 (1904); **340**, 1 (1905).

water, and finally to precipitate the nitrite with ether; it was afterwards recrystallized once or twice from acetic ester. Wallach gives 112° to 113° as the melting point of the substance while Schreiner found 120° to 121°. During the first work which I did with this substance it was recrystallized from hot solvents and the melting point seemed to depend somewhat upon the solvents used. When acetic ester was employed the final melting point was always 113° to 115°. It was finally found that by dissolving the nitrite in acetic ester at 30° and then crystallizing in a freezing mixture, the melting point given by Schreiner was obtained. When the pure α-nitrite was again recrystallized from hot acetic ester, its melting point was lowered to about that found by Wallach. The latter used hot acetone in purifying his product, and the low melting point does not indicate that the substance with which he worked was impure. The conclusions drawn by Wallach from his work with this substance are based upon the assumption that it was free from chemical or physical isomers.

Rotation of the Nitrite.—The optical rotation found by Wallach for the α-nitrite obtained from two different sources was considerably higher than that found by Schreiner. In fact, the numbers given by Wallach for the same product show a considerable variation. Both workers used chloroform as a solvent. By the use of the same solvent I obtained a value agreeing very closely with that of Schreiner, the solution having stood for about ten minutes before the reading was made. It was found later that the reading diminished quite rapidly on standing.

(1) A solution of 0.35 gram of pure α-phellandrene α-nitrite, dissolved in 5 cc. of pure chloroform (Kahlbaum, best quality, shaken out repeatedly with water, dried over calcium chloride and then distilled), lost its optical activity entirely after standing for about four hours. The solvent was evaporated *in vacuo*. The residue did not crystallize until a small amount of ether was added, which evidently dissolved out some amorphous decomposition products. The recovered product, which was fully three-fourths of the amount used originally, was again dissolved in 5 cc. of fresh chloroform and

the solution was now found to be slightly levorotatory, the value being about one-tenth that of the original.

(2) A solution of 0.3 gram pure α-nitrite in 10 cc. of chloroform, after standing for eighteen hours, showed a positive rotation equal to about one-half that of the original negative value.

(3) A solution of 0.5 gram of pure α-nitrite in 3 or 4 cc. of chloroform was allowed to stand overnight. The chloroform was then removed, for the greater part, *in vacuo* and the residue treated with a small amount of ether. The solid residue was pressed out on a porous plate and again washed with ether. It consisted of a little more than 0.3 gram. When recrystallized from acetic ester it melted at 120° to 121° and the rotation of the recrystallized substance, roughly determined in dilute chloroform solution, was found to be about the same as that of the original pure α-nitrite.

(4) A saturated solution of the pure nitrite in acetic ester showed $\alpha_D = -6°.2$. A reading made some time later demonstrated that the rotation of the solution was decreasing. After standing overnight it had changed to $+1°.8$. The solvent was then removed *in vacuo* and the residue washed well with ether, only about one-fourth of the weight of original nitrite remaining. When this was recrystallized from acetic ester it melted at 119°.5 to 120°.5 and showed a rotation approximately the same as the original.

From the above experiments it seems certain that the change in rotation is not caused by a change of the dextro- into levo-α-nitrite, although, otherwise, the results obtained do not appear at all clear.

Wallach has shown that there is no change in melting point when the dextro- and levo-α-nitrite are mixed; hence the racemic mixture appears to be very similar to the active forms. It was desired to determine whether the varying rotation found for different samples of phellandrene could be explained by the presence of the racemic modification and it was thought that this could be determined from the rotation of the purified nitrite. In the case of the nitrite from oil XVII,A, purified, the value $[\alpha]_D^{30} = -126°.8$ at a concentration of 12.3 was

found. The nitrite obtained from XIV,A, purified, gave $[\alpha]_D^{30} = -124°.5$ at a concentration of 8.84 Both readings were taken about ten minutes after the solutions were made, and from the rate at which the rotation was found to decrease, the immediate values would be about those found by Wallach. From this there appears to be no evidence that any racemic form of phellandrene is present in either of the two oils, the first of which had a value $\alpha_D^{30} = +73°.5$, and the second, $\alpha_D^{30} = +105°$. Later, another cause was discovered for this varying rotation of the phellandrene oils.

Stability of Phellandrene.—Wallach[1] recognized the fact that phellandrene is not a stable substance and recommended that it be fractioned *in vacuo*. Nothing further on the subject is to be found in the literature. It was ascertained that by distilling a sample of phellandrene at ordinary pressure, the rotation was lowered about 2°.

(1) The distilled product just mentioned was heated in a tightly stoppered distilling flask in an oil bath at 190° for eight hours, then distilled from the flask; about one-fifth of the total remained as a viscous residue almost insoluble in alcohol. The oil redistilled from 172° to 174°, which is a little higher than the boiling point of the original. Its rotation had decreased from +105° to +70°.

(2) The last distillate obtained was then sealed in a hard-glass tube and heated in an oven for twenty-four hours at 250°. The product was colored a slight yellow. It was distilled with steam, about 15 per cent of nonvolatile matter remaining behind. The distillate showed $\alpha_D^{30} = -25°.5$. It distilled completely from 171° to 176°.5. Phellandrene was no longer present and after careful trials no other terpenes could be identified. The oil had a very peculiar, benzenelike odor, which was quite different from that of any other terpene.

(3) The experiment was repeated with a fresh amount of the original sample of phellandrene. This time the heating was carried on at 225° for twenty-four hours. The product was colored slightly yellow. It was distilled with steam, a residue of nearly 25 per cent remaining behind. The distil-

[1] Ann. Chem. (Liebig), **287**, 372 (1895).

late had the same peculiar, benzenelike odor and gave a very slight test for phellandrene. $\alpha_D^{30} = -23.8$. It distilled completely from 171°.5 to 176°.5 and appeared to be identical with the product obtained in the last experiment.

(4) The combined residues obtained in this and the preceding experiments were distilled at 10 or 15 mm. A suitable thermometer was not used, so that the result of the distillation could be only roughly judged. A small amount of terpene oil passed over first, then a quantity of higher-boiling, somewhat viscous oil distilled before the temperature had risen much beyond 200°. Later, decomposition set in, the temperature went much higher, and the distillate was very viscous. It appears certain, however, that one of the polymeric products of phellandrene, probably a diterpene, may be distilled without decomposition.

In order to obtain evidence as to whether or not phellandrene is converted into the racemic form by heating, a quantity of very pure phellandrene (XVI,A, purified) was heated in a sealed tube at 200° for ten hours.

The product was distilled with steam and the distilled oil showed $\alpha_D^{30} = +38°$. Phellandrene nitrite prepared from this in the usual manner melted at 119° to 120°.5 after the first recrystallization from acetic ester. In chloroform solution, at a concentration of 3, the specific rotatory power was found to be about the same as that produced in previous cases by the α-nitrite, and therefore there was no evidence that any racemic phellandrene had been formed.

After what has been brought out concerning the rapid change in rotation which the nitrite undergoes in solution, it must be borne in mind that the values obtained for this property of the nitrite are only approximate, but when they are taken for different samples under the same conditions, they are abundantly adequate for purposes of comparison.

The phellandrene used in the heating experiments (1), (2) and (3) was taken from sample XIV,A, purified, which, as will be brought out later, contained a small amount of levolimonene. The process was therefore repeated with a quantity of XVI,A, purified, which, so far as it was possible to de-

termine, was pure phellandrene. The substance was heated in a sealed tube for forty-eight hours at 210° to 215°. The product was colorless. The oil, after having been distilled with steam, still gave a slight test for phellandrene and showed $\alpha_D^{30} = -18°$. The levorotation of the product appears, therefore, to be due to a product of isomerization of phellandrene. This oil, when dissolved in cold carbon tetrachloride and treated with bromine, combined at once with less than 2 atoms of the latter and considerable hydrobromic acid was evolved. Further action was much slower. The same result was obtained in glacial acetic acid, although in this case the evolution of hydrobromic acid was not so apparent, as it was probably held in solution by the acetic acid.

A portion of the same sample of freshly purified phellandrene used in the last experiment was sealed in a flask which was nearly full and allowed to stand for three months. The original rotation was $\alpha_D^{30} = +129°.8$. On opening the flask it was found to be $\alpha_D^{27.5} = 127°.1$, hence a decrease of about 3°. Phellandrene, therefore, undergoes a slow alteration at ordinary temperatures, probably the same which takes place more rapidly at a higher temperature.

Action of Hydrochloric Acid.—About 30 grams of phellandrene, taken from the oil V,A, purified, were heated with metallic sodium for a few minutes, then distilled from the metal into a dry fractioning flask. $\alpha_D^{30} = +115°.5$. It was mixed with an equal volume of dry carbon disulphide and a slow stream of very dry hydrochloric acid was then passed into the liquid, the exit tube having been attached to a tube of calcium chloride. The acid was readily absorbed and the liquid appeared to become heated more quickly than when limonene had been employed under the same conditions. It was kept cool by immersing the flask in a dish of water. After four or five hours, the absorption appeared to be nearly complete, but the current of acid was continued for several hours longer. The contents of the flask were then distilled at reduced pressure. After the excess of acid and the carbon disulphide had been removed, the residue was distilled at as low a pressure as could be maintained, considering that hydrochloric

acid appeared to be given off continually. The product distilled completely within a range of 15° or 20°; the distillate contained much terpene and possessed a very strong odor of hydrochloric acid. Phellandrene behaves quite differently from limonene, and the hydrochloride which appears to be formed at ordinary temperature is decomposed to a large extent by distillation at reduced pressure.

Action of Bromine.—Several investigators have studied the action of bromine upon oils containing phellandrene, and from their work it appears that the substance takes up at once only 2 atoms of bromine to form an oily dibromide. It was desired to ascertain whether this dibromide, when prepared from pure phellandrene, could be obtained in the crystalline form.

Three and one-tenth grams of phellandrene, taken from sample XVI,A, purified, were dissolved in 3 volumes of carbon tetrachloride and the solution cooled in a freezing mixture; 3.4 grams bromine (2 atoms), dissolved in 3 volumes of the same solvent and cooled, were then slowly added to the first solution, which was continuously shaken, while immersed in the freezing mixture. The color of the bromine disappeared immediately, until nearly all had been added; the last few drops produced a color which remained for over one minute and fumes of hydrobromic acid then appeared. The solution was then evaporated *in vacuo* for several hours in order to remove the solvent completely. The residue, a quite mobile oil, was allowed to remain in the ice chest for twenty-four hours, but did not crystallize.

Crystalline Auto-oxidation Product of Phellandrene.—It was frequently observed that samples of purified oils, on standing, deposited crystals upon the walls of the containing vessel. The same thing has been noted, in working with elemi oil, by Tschirch and Cremer and also by Wallach, who connected the crystals with the solid constituents of the resin. In most cases, even after long standing, the amount of crystalline substance was small in proportion to that of the oil, but in several instances about 0.2 gram was obtained from 50 to 75 grams of oil. One sample of purified, high-boiling oil, not

over 25 grams in amount, deposited nearly 0.5 gram of this crystalline substance soon after distillation. It was later observed that in no case were crystals found in an oil derived from a sample of elemi known not to contain phellandrene. Although, at this time, some of the oils had been completely used up, it was observed that more or less of the crystalline substance could be found in both the terpene and the high-boiling oils on hand which were derived from samples containing phellandrene. It seems almost certain that the substance is derived from phellandrene. In all cases which were studied, the crystals from different oils were found to be identical. They are moderately soluble in alcohol and acetic ester, sparingly in ether and chloroform, and almost insoluble in petroleum ether. They are best purified by recrystallization from hot acetic ester, from which solvent they separate, on cooling, as fine needles, melting at 164°.5 to 165°.5. In most cases they were pure after the first crystallization. In the condition in which they are found in the oil, the crystals are colorless, hexagonal prisms, generally of good size; two of the largest weighed, when taken together, just 1 centigram.

I. 0.1667 gram substance gave 0.4322 gram CO_2 and 0.1607 gram H_2O.

II. 0.0713 gram substance gave 0.1853 gram CO_2 and 0.0708 gram H_2O.

	Required for $C_{10}H_{18}O_2$.	Found. (1).	(2).
C	70.59	70.71	70.87
H	10.59	10.71	11.03

The substance is probably a dihydroxyphellandrene. That it is of the simple formula given, rather than a polymer, is indicated by the fact that it sublimes very readily when it is heated below its melting point.

As to the physical constants of phellandrene, the values obtained from XVI,A, purified, should be given preference. Those of several of the other samples, most of which, it will be seen later, contain small amounts of levolimonene, are also given in the following table, there being, of course, very little difference except in the degree of rotation.

Purified product.	Boiling point, complete.	α_D^{30} +	n_D^{30}	Sp. gr. $\frac{30}{4}$	Boiling point at reduced pressure.	mm.
XVI,A	172–173.5	129.8	1.4695	0.8324	89.3–90.8	56.5
V,A	172–174	122.6	1.4698	....	82.7–84	43.5
XIV,A	.....	105.1	1.4694	0.8322		
XVIII,A	172–173.5	113.5	1.4696	0.8330		

Each of two determinations gave the specific gravity at $(\frac{30}{4})$ as being 0.0075 less than that at $(\frac{20}{4})$.

The boiling point of phellandrene is seen to be about 4° lower than that of limonene; the specific gravity is a little less, while the index of refraction is somewhat higher.

In determining the constitution of phellandrene, Wallach[1] has recently deduced the molecular refraction of the substance, deriving his value from the phellandrene obtained from elemi oil by fractionation. From the present work it can be seen that this "phellandrene" was partly limonene, although it can also be seen that the limonene would have little influence upon the value obtained.

Classification of the Terpene Oils.

(1) Of the 21 samples of resin examined, 10 gave pure dextrolimonene.

(2) Nine of the remaining oils, including all but the two optically inactive ones, contained more or less phellandrene. These nine oils fall into two classes.

(*a*) Those showing an initial boiling point decidedly lower than that of phellandrene and possessing a peculiar, indefinable odor. These are the oils from *Samples VII.*, *X.* and *XV.*, and all are dextrorotatory. The oil from *Sample X.* has the lowest initial boiling point and its rotation is decidedly the smallest. The data obtained for the physical constants of these oils do not lead to any decided conclusion, but it appears extremely improbable that any body like pinene is present in them. From the marked regularities which are found to exist in the different samples, it seems very probable that we have present in these three cases one of the unidentified terpenes of the limonene series.

[1] *Loc. cit.*

(*b*) Of the remaining six oils containing phellandrene, obtained from *Samples V., XI., XIV., XVI., XVII.* and *XVIII.*, one was levorotatory, and the others, although they were all highly dextrorotatory, showed considerable variation in rotation. The two giving the greatest variation also had a slightly higher boiling point, while the others, to judge from their boiling point, appeared to be pure phellandrene. As has already been brought out in the discussion of *Sample XI.*, the terpene oil derived from it consisted largely of levolimonene.

In summing up this work it was suspected that the variation in the rotation of the other phellandrene oils was due to the presence in them of small amounts of levolimonene which could not be detected. As shown in the experimental work which is detailed just below, the presence of levolimonene could readily be proved by the addition of a small portion of dextrolimonene to the oil and the subsequent isolation of dipentene tetrabromide. The presence of levolimonene was proved in oils XVII,A, purified, and XVIII,A, purified. XIV,A, purified, had been used up in previous work. In V,A, purified ($\alpha_D = +122°.6$) and XVI,A, purified ($\alpha_D = 129°.8$), it cannot be definitely concluded whether or not levolimonene was present, and it can be readily seen that if present at all it was in very small amounts.

Detection of Levolimonene.—A portion of XVII,A, purified, was added to one-tenth its weight of dextrolimonene and 0.45 gram of the mixture was treated in a freezing mixture with bromine in amyl alcohol and ether. Crystals soon began to separate, and after 3 hours they were filtered and washed with a small amount of alcohol. The yield was 0.65 gram. After one recrystallization from a mixture of alcohol and acetic ester, the product melted at 124° to 125° and was, therefore, dipentene tetrabromide.

Four grams of XVIII,A, purified, were mixed with 0.4 gram of dextrolimonene and treated with bromine as before. After the product had stood overnight, 0.2 gram of crystalline bromide was obtained, this being only about one-third of the amount isolated in the previous case. After recrystallization from a mixture of alcohol and acetic ester the body melted

at 124° to 125° and was accordingly pure dipentene tetrabromide.

Both V,A, purified, and XVI,A, purified, the former, at least, presumably containing a very small proportion of levolimonene, were treated with 15 per cent of their weight of dextrolimonene and brominated in the usual manner. In neither case had a trace of the crystalline product separated after twenty-four hours, but in each instance, after two or three days, a small quantity of crystals appeared which, after recrystallization, melted at about 124°. No great significance is attached to this for it was found that XVII,A, purified, when it was brominated without the addition of limonene, after standing for several days, yielded a very small amount of crystals which had about the same melting point; the appearance of dipentene tetrabromide in these cases is possibly due to the continued action of hydrobromic acid upon limonene tetrabromide.

(3) The two remaining samples of resin gave almost optically inactive oils, which were found to be terpinene and terpinolene.

High-boiling Oils.

The high-boiling oil contained in distillates B and C of the resin was found in most cases to consist chiefly of a constant-boiling product. By distilling twice *in vacuo*, a number of such products were obtained and it was found that the boiling point was almost the same in all cases, 167° to 170° at 35 mm. In some cases it was 1° or 2° higher or lower. In all of their other properties, however, these oils showed marked differences. The data derived from them are placed in the table below in order to make plain the relation existing between them.

In this table every measurement which has been made is recorded. In a few cases, especially with the older samples of resin, it was found impossible to obtain a constant-boiling product from the crude distillate, and in other instances no high-boiling distillate was taken.

Designation of oil.	Sp. gr. $(\frac{30}{4})$	α_D^{30}	n_D^{30}	Appoximate solubility in 100 parts 55 per cent alcohol (by volume).
IV,C, purified	1.0315	—1°.2	1.5159	16
I,C, purified	1.0247	±0°.0	1.5143	....
XIII,B, purified	0.9969	—0°.5	1.5068	....
III,B, purified	0.9887	—2°.5	1.5055	7.5
VII,C, purified	0.9689	—2°.5	1.5005	....
VI,B, purified	0.9621	.... [1]	1.4995	....
VIII,B, purified	0.9559	—2°.4	1.4985	4
XVIII,B, purified	0.9559	+2°.0	1.4950	....
II,C, purified	0.9522	—2°.7	1.4973	....
XIV, B, purified	0.9482	—2°.0	1.4957	....
XVI,B, purified	0.9461	—0°.8	1.4944	3
XII,B, purified	0.8677	+71°.6	1.4757	3

The oils are arranged in the order of their specific gravities and it will be seen at once that the indices of refraction arrange themselves in precisely the same way, with the exception of XVIII,B, purified, which has an index about 0.0035 lower than it should have. This same oil is also exceptional in that it is slightly dextrorotatory, while all the others are slightly levorotatory. All the oils are practically optically inactive excepting XII,B, purified, which stands apart in all respects from the others.

Analyses of XII,B, purified, gave the following results:

I. 0.1455 gram substance gave 0.4309 gram CO_2 and 0.1503 gram H_2O.

II. 0.1490 gram substance gave 0.4405 gram CO_2 and 0.1534 gram H_2O.

	Required for $C_{15}H_{26}O$.	Found. (1).	(2).
C	81.08	80.77	80.63
H	11.71	11.48	11.44

The analyses are in tolerably good agreement with the formula assigned. The substance, which had remained as an oil for three months after purification, became solid when the inside of the bottle was scratched with a glass pipette. It dissolved in all the organic solvents in any proportion and when

[1] Not determined.

an attempt was made to recrystallize it from dilute alcohol in the cold, it separated as an oil. The body is almost colorless and possesses a mild, pleasant odor. It is moderately viscous. At ordinary pressure it distils at 270° to 280° with the formation of water.

A half-dozen or more substances containing oxygen, mostly crystalline, have been isolated from the high-boiling portions of different essential oils. They have, in general, the same properties as this body, and to most of them the same chemical formula has been assigned. They are sometimes known as sesquiterpene alcohols. To judge from the data given in the above table, the body is radically different from any of the other constant-boiling products isolated from different samples, and, as will be seen later, it is not a constituent of any of these oils. It is evidently practically a pure substance and its occurrence in this single sample is most remarkable.

All of the other oils given in the table are closely related and are grouped together. In addition to the regular variations already noted, there is a constant increase in viscosity from the first oil to the last. The first, IV,C, purified, is very mobile, while the last, XVI,B, purified, is very viscous. All of these regularities at once suggest that we have in these different products a mixture of two substances in varying proportions and this is undoubtedly the case. The following analyses tend to confirm this view. The values obtained for XVI,B, purified, are as follows:

I. 0.1911 gram substance gave 0.5533 gram CO_2 and 0.1934 gram H_2O.

II. 0.1630 gram substance gave 0.4721 gram CO_2 and 0.1637 gram H_2O.

	Found.		
	(1).		(2).
C	78.96	—	79.00
H	11.24		11.16

The analysis of XIV,B, purified, gave the following results:

I. 0.1482 gram substance gave 0.4286 gram CO_2 and 0.1460 gram H_2O.

II. 0.1580 gram substance gave 0.4547 gram CO_2 and 0.1589 gram H_2O.

III. 0.2116 gram substance gave 0.6132 gram CO_2 and 0.2137 gram H_2O.

	Found.		
	(1).	(2).	(3).
C	78.87	78.49	79.03
H	10.95	11.17	11.22

The values obtained for III,B, purified, are as follows:

I. 0.1683 gram substance gave 0.4629 gram CO_2 and 0.1533 gram H_2O.

II. 0.1714 gram substance gave 0.4709 gram CO_2 and 0.1500 gram H_2O.

	Found.	
	(1).	(2).
C	75.01	74.93
H	10.12	9.72

IV,C, purified, gave the following values:

I. 0.1504 gram substance gave 0.3917 gram CO_2 and 0.1163 gram H_2O.

II. 0.1887 gram substance gave 0.4917 gram CO_2 and 0.1420 gram H_2O.

III. 0.2388 gram substance gave 0.6245 gram CO_2 and 0.1850 gram H_2O.

	Found.		
	(1).	(2).	(3).
C	71.03	71.07	71.32
H	8.59	8.36	8.79

Analysis III. was made on a middle fraction of the substance, redistilled in a vacuum.

If we consider that these oils belong either to the terpene or sesquiterpene class, and are composed of substances having the formula $C_{10}H_{16}$ or $C_{15}H_{24}$, or of their oxygen derivatives, and consider also their boiling points, we have, in general, three possibilities: (1) a sesquiterpene, or (2) a dioxygen derivative of a terpene, or (3) a monoxygen derivative of a sesquiterpene may be present. The sesquiterpenes are almost insoluble in dilute alcohol; the solubilities in 55 per cent alcohol (by volume), respectively, of pure cadinene prepared from the hydrochloride and pure cedrene distilled from oil of cedar were determined and found to be practically *nil*. The differ-

ent high-boiling oils from elemi were then tested with the result that they showed a considerable solubility in 55 per cent alcohol; this solubility, which, in several instances, is given in the table, varied just as do their other properties. In a few instances there was evidence of a trace of sesquiterpene, but the amount was inconsiderable. That the soluble constituents of the oil would have no great effect upon the solubility of a sesquiterpene, if such a substance were present, was shown by adding a small amount of the latter to several of the clear solutions.

The solubility of oil XVI,B, purified, the last one of the series, is very close to that of the pure sesquiterpene alcohol XII,B, purified (see p. 645), so that the assumption that we have here a substance similar to the latter seems to be verified. Moreover, the analysis of XVI,B, purified, shows that its composition is close to that of a sesquiterpene alcohol. On the other hand, the member at the other extreme of the series IV,C,purified, has a much greater solubility in 55 per cent alcohol, this property being remarkable. Considering the analysis and the boiling point, the latter substance appears to be a dioxygen derivative of a terpene and is nearly pure; all of its properties are in accord with this assumption. The values obtained on analysis show so great a difference from any formula which can be calculated for the oil that it cannot be considered pure. The formula $C_{10}H_{14}O_2$ requires 72.28 per cent for carbon and 8.44 per cent for hydrogen. This oil is slightly yellow in color, of a very mild, pleasant odor, and is perfectly miscible with all the solvents. It redistilled from 275° to 279° at ordinary pressure, with the formation of water.

The other oils are all more or less yellow in color. Because of the great viscosity of the oils in the lower part of the series and also because of their lack of optical activity, it seems certain that the sesquiterpene derivative contained in them is quite different from the optically active substance XII,B, purified.

Amyrin.

The crystalline residue obtained from elemi by treating it with alcohol has been worked with by many chemists and has

long been known as amyrin. Baup,[1] who appears to have employed Manila elemi in his work, gives 174° as the melting point of the substance. Vesterberg,[2] who also used Manila elemi, was unable to obtain a constant melting point and showed that the substance is a mixture of two very similar bodies, which were separated by means of their acetyl derivatives; these bodies are α-amyrin, melting point, 180° to 181°, and β-amyrin, melting point, 193° to 194°. Tschirch and Cremer give 170° to 171° as the melting point of amyrin from Manila elemi after repeated crystallization.

I wished to note if there was any variation in the amyrin obtained from individual samples of elemi; it was thought that possibly α-amyrin or β-amyrin might be found in pure condition, when derived from the resin of a single tree.

Two samples, VIII., from which had been isolated pure limonene, and XVIII., which had yielded almost pure phellandrene, were examined. In neither case could a body of constant and sharp melting point be obtained; the products resulting from several recrystallizations behaved as mixtures, although, comparatively, they melted at about the same temperature.

This work was carried on in Manila in the chemical laboratory of the Bureau of Science of the Philippine Government.

ON THE THEORIES OF INDICATORS.

By S. F. Acree.

In a conference, Professor Stieglitz has convinced me that his attitude towards the chromophoric theory of indicators, as expressed in his article of 1903, has remained the same as that which he postulated in our interview in September, *viz.*, that the idea of simple quinoid chromophores requires amplification on the basis of intermolecular quinhydrone formations for phenolphthalein, rosaniline and similar dyestuffs. He has shown me now that his refutation, in his March

[1] Jahres. d. Chem., **1851**, 528.
[2] Ber. d. chem. Ges., **20**, 1243 (1887); **23**, 3187 (1890).

article,[1] of my charge of "wrong ideas" was limited to the alleged "wrong idea" of overlooking the ionization of the phenol groups in phenolphthalein. It is clear now, from a statement of his experimental work, not yet published, that he includes the phenol salts of these indicators in his quinhydrone hypothesis. I was not aware of that fact when I wrote the April article.[2] Professor Stieglitz therefore developed the idea of quinhydrone formation in such types as rosolic acid, alizarin, eosin, phenolphthalein, etc., as I pointed out in April,[3] and from this developed the idea of the quinhydrone salts. Professor Stieglitz credits me for the idea of tautomeric mono- and dibasic salts of phenolphthalein, etc., and for the development of the idea of quinhydrone salts, suggested by Baeyer[4] and Hantzsch,[5] from our idea of tautomeric salts and the work of Baeyer,[4] Hantzsch,[5] Baly,[6] and Jackson and Oenslager[7] and Jackson and Clarke.[8] It is evident, therefore, that we reached similar conclusions from these two different starting points.

The similarity of our views concerning the constitution of these colored salts, as well as the points of difference, make it seem best that my April article be considered a joint article by J. Stieglitz and S. F. Acree, expressing the independent views and conclusions of each of us, and I request that it be reviewed and indexed as such. Mr. Stieglitz has agreed to this arrangement, proposed by me as soon as my attention was called to the true circumstances. By agreement I shall investigate the problem chiefly from the standpoint of the alkylation reactions and Professor Stieglitz is investigating the color phenomena as affected by the equilibrium conditions, the need for which was brought out by me in April.

JOHNS HOPKINS UNIVERSITY,
April 25, 1908.

[1] THIS JOURNAL, **39**, 429.
[2] *Ibid.*, **39**, 528.
[3] *Ibid.*, **39**, p. 529, footnote.
[4] Ann. Chem. (Liebig), **354**, 162 (1907).
[5] Ber. d. chem. Ges., **39**, 1089, 1095, 3076, 3080 (1906); *Ibid.*, **40**, 333, 1527 (1907).
[6] J. Chem. Soc., **83**, 1029; **89**, 502, 514; **91**, 426, 1572.
[7] THIS JOURNAL, **18**, 1.
[8] *Ibid.*, **34**, 441.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

THE THEORY OF INDICATORS.

By Julius Stieglitz.[1]

Professor Acree, in his article on the Theory of Indicators,[2] has brought out quite thoroughly and sufficiently the reasons which lead me also to the conclusion that the chromophoric theory of indicators (the "simple quinoid theory," as it may be termed for convenience), as given in my article in the *Journal of the American Chemical Society* in 1903,[3] required amplification, and that it required amplification on the basis of the idea of intramolecular quinhydrone combinations for phenolphthalein, rosanilines and similar indicators and dyestuffs.[4]

By some misunderstanding—our discussion of the subject was comparatively brief—Dr. Acree did not know that I included in the quinhydrone hypothesis the effect of alkalies as intensifying the color of phenol indicators (rosolic acid, etc.), as they do that of quinhydrones. This fact being one of daily experience with me—I had been working for two years with alizarin, alizarinsulphonate and rosolic acid—was not emphasized by me, but taken for granted. It was really one of the main reasons for my not being satisfied with the old "simple quinoid hypothesis;" the latter did not include any rational explanation of the intense change of tint of this class of indicators when alkali is added. In alizarins, rosolic acid, etc., we have a quinoid group *ab initio* and yet the color is enormously intensified by the addition of alkali. This effect was formerly considered to be due simply to "auxochromic" influence of the phenol groups and their salts, according to the current ideas, without any attempt to develop an explanation of such well-known "auxochromic" results. The quinhydrone hypothesis seemed to me the most rational explanation of this change of color because I was familiar with Jackson's important observa-

[1] See the preceding article in this number of This Journal.

[2] *Ibid.*, **39**, 528 (1908).

[3] **25**, 1119.

[4] This Journal, **39**, 431, footnote. *Ibid.*, **39**, 529, footnote 2, first two lines.

tion[1] that the alkali salts of quinhydrones (phenoquinones) are even more intensely colored (blue) than are the corresponding quinhydrones themselves; this observation had been impressed on me so much the more since in his first paper Jackson refers to my work[2] on a related compound, dichlorquinonedimalonic ester, a body which in 1891 I had found to change from a pale-yellow tint to permanganate purple when treated with alkali, and to a deep blue when treated with ammonia. It was the combination of these results of Jackson's with the well-known characteristic behavior of rosolic acid and also with the behavior of the phenol and carboxylic esters of phenolphthalein and its derivatives that ultimately led me to the conviction that intramolecular quinhydrone formation is really the cause of the intense coloration of our phenol derivatives when used as indicators with alkalies. Another possibly important factor has been brought out recently by Torrey's[3] and Hantzsch's[4] investigations on the colored phenol silver salts. Green's[5] discovery of last September that the carboxyl ester of phenolphthalein is orange and that alkalies convert it into a violet salt confirmed me, it may be said, in my conclusion that I was on the right track:

$$O{:}\,C_6H_4{:}\,C(C_6H_4OH)C_6H_4COOCH_3,^6 \text{ orange;}$$

$$\overline{O{:}\,C_6H_4{:}\,C(C_6H_4ONa)C_6H_4COOCH_3},^7 \text{ violet.}$$

I will not take space here to dilate on my views concerning the quinhydrone hypothesis, but will reserve this to a more fitting occasion; I agree in the main points with the development of the equations by Professor Acree.[8] I will say, however, that an adequate theory must account for the greater intensity of color of quinhydrones *versus* simple quinones;

[1] THIS JOURNAL, **17**, 588; **18**, 1, etc.

[2] *Ibid.*, **13**, 38 (1891).

[3] Torrey and Hunter: Ber. d. chem. Ges., **40**, 4332 (1907).

[4] Hantzsch and Scholtze: *Ibid.*, **40**, 4875 (1907).

[5] Green and King: *Ibid.*, **40**, 3724 (1907).

[6] This is probably an intramolecular quinhydrone in equilibrium with the body of the structure given, as is probably the case for rosolic acid.

[7] This probably has a modified structure, involving the formation of a *second quinoid complex* of the phenolate group.

[8] *Loc. cit.*

it must account for the still greater intensity of color of the metal salts of the quinhydrones, and also for the significant fact recorded by Jackson that aliphatic alcohols form *colorless* addition products with quinones; in that last fact lies, I believe, the key to the correct solution of the whole problem, the necessary second (and third) phenol groups giving us the nuclei for the formation of new (quinoid) chromophores. Only extensive qualitative and particularly quantitative work on the questions of equilibrium and stability involved can give the necessary experimental basis for a final solution, as has also now been brought out by Acree. It was the wish to bring such experimental material which has delayed the publication of my views—a result now accomplished by the joint paper with Professor Acree.

REPORTS.

IONIUM, THE PARENT OF RADIUM.

A Review of Recent Investigation.

It has always been felt necessary to suppose that the continual breaking down of radium into radium emanation and α-particles is compensated, in the natural ore, by a continual regeneration; in fact that the supply is kept up by the breaking down, also continuous and spontaneous, of another substance by which radium is produced. The existence of radium at the present day presupposes a parent, as the perturbations of Saturn predicted the undiscovered Uranus and Neptune.

It is true that the rate of decay of radium is so slow, compared to the duration of laboratory experiments, as to be almost negligible, yet in proportion to the hundreds of thousands, or millions, of years by which geologists measure the age of deposits, it is so rapid that no original supply of radium, even in veins of pleistocene age and all but the most recent of the 'recent' formation, could have survived to the present time. If we take the highest estimate for the decay period, *i. e.*, that about 3000 years is required for any quantity of radium to be reduced to one-half, it is easily seen that as the decay follows an exponential law, in $x \times$ 3000 years the amount will be reduced to $\frac{1}{2^x}$. Putting, for example, $x = 22$ we see that in 66000 years a mass of ore which was

originally pure radium would be reduced to a content of about one part in four millions, or a quarter of a gram per ton, which is about that of the richest pitchblende as it now exists, while in another 60,000 years this minute amount would be again reduced a million times. It is plain then that radium itself must be a link in a chain of radioactive disintegration, such as has been fully investigated in the case of the more quickly decaying radium emanation and its products, radium A, B, C, D, E and F. As in that case, so here, each member of the series accumulates by the breaking down of its predecessor until its own rate of decay exactly counterbalances its formation, after which the amount present remains in a constant proportion to the amount of its parent. The proportion of substances in this state of *radioactive equilibrium* must obviously be the inverse of that of their rates of decomposition (or directly equal to that of their decay periods) and the time taken to reach a state of practical equilibrium may be put at about ten times (since $\frac{1}{2^{10}}$ is slightly less than 0.1 per cent) the decay period of the substance formed.

With the help of this theorem we can readily determine the amount of radium in any substance by measuring the activity of the emanation which exists in it in radioactive equilibrium, provided that the substance has not been subjected to chemical treatment for a previous period of about forty days (the decay period of the emanation being 4 days). Analyzing in this way twenty-two specimens of uranium ores containing from 0.3 to 75 per cent of uranium, Boltwood found a strikingly constant proportion between the amounts of uranium and radium present.[1] His conclusion confirmed a previous suggestion by Rutherford and Soddy[2] that radium was formed by the decomposition of uranium. The constant proportion, itself a necessary consequence of the law of radioactive equilibrium, could be satisfactorily accounted for in no other way.

Since every gram of radium is accompanied by nearly three million grams of uranium, it follows that the latter decays so slowly, taking over a thousand million years to fall to half its value, that we may regard its amount as approximately constant throughout geological time. So delicate however, is the electroscopic method of testing for radium that as little as 10^{-12} gram can be detected with reasonable certainty, an amount which should be generated by a kilogram of uranium, when in radioactive equilibrium, in about

[1] Phil. Mag. [6], **9**, 599 (1905).
[2] *Ibid.* [6], **5**, 590 (1903).

a quarter of an hour. This was tested by Soddy, Whetham and Boltwood, using different methods to purify their uranium, with varying results. One fact was, however, made plain by all three, that the rate of growth was certainly far below, and probably less than a thousandth part of the value just calculated. The necessary conclusion is that uranium does not generate radium directly, but first produces an intermediate product with a fairly slow rate of decay. Not till this has accumulated for many years, perhaps centuries, will radioactive equilibrium be established and the rate of growth of radium reach the above value. The known transition product, uranium X, with its small decay period of 22 days, does not materially affect the question; for slow changes we may regard the decay of uranium X as if it were identical with the uranium whose history it so closely follows.

Researches actively carried on in several quarters for the last three years in the hope of finding this missing link have recently been crowned with success. Boltwood announced[1] in November, 1906, that he had isolated from a uranium mineral a small quantity of a substance, which he took to be actinium,[2] which more than doubled its radium content in six months. Starting with the precipitate carried down by a little thorium oxalate in a solution of 1 kg. of carnotite, a rate of growth of radium was observed equivalent to 1.6×10^{-8} gram per year. This would suffice to maintain equilibrium with the 7.6×10^{-5} gram radium which, by calculation, existed along with the 200 grams uranium in the ore, if the decay period of radium is 3100 years, which agrees closely with other determinations.[3] This would show that the immediate parent of radium was present in the precipitate. Rutherford[4] confirmed this observation but pointed out that the substance in question could not be actinium, owing to the insufficient activity of the latter on the hypothesis that all the radium in ores is derived from it. For the activity of any substance in radioactive equilibrium must bear a fixed proportion to that of any other substance in the series, and this proportion can be approximately calculated from the number of steps in the series of changes in which α-particles are given off. For the velocity of these particles, the chief cause of the ionization of the air observed by the electroscopic test, does not vary greatly, while the number lost from a molecule at

[1] Nature, **75**, p. 54.

[2] Identical with Giesel's "Emanium." Debierne: Compt. rend., **139**, 538 (1904).

[3] Ramsay and Cameron (J. Chem. Soc., **91**, 1266 (1907)) alone find a decidedly lower value, about 200 years.

[4] Nature, **75**, 270.

each change in which they are expelled is constant (probably *one* each time). Now, as we have seen, in a state of equilibrium the same number of molecules of *each substance* is formed and destroyed per second, the greater or slower rate of decay of the several substances being exactly compensated by the smaller or larger proportion in which they are present. Thus, for example, the activity of radium and its products of decomposition, four of which give out α-particles, must together be about five times that of the same radium when freshly prepared, a proportion which agrees with experimental determinations. Now the activity of the actinium present in a uranium mineral is only a small fraction of that of the radium. Again the last known product of actinium degradation, Act. B, failed in Rutherford's hands to give more than a fifth, at most, of the calculated quantity of radium. In a later letter[1] Rutherford states that he has separated from his actinium by ammonium sulphide a fraction about 100 times as active as the original preparation, yet showing no appreciable growth of radium in 80 days. The radium parent, therefore, a substance chemically quite distinct from actinium, accompanies the latter in commercial specimens, and is more readily carried down by the sulphur precipitated from the thiosulphate in the (old?) ammonium sulphide. Radioactinium, the first product of the decay of actinium[2] and the probable cause of all its activity, is also relatively more concentrated in the precipitate, causing a rise of activity to twice its value in 20 days; but no corresponding change in the rate of growth of radium could be detected. Boltwood[3] accepts Rutherford's conclusion, confirming it by showing that 0.4 gram of a preparation of his new substance some weeks after separation, "sufficient to give a leak of 500 div. per min. in an α-ray electroscope, did not produce sufficient actinium emanation to permit its detection in another electroscope of greater sensitiveness." No rise in activity was observed corresponding to the formation of actinium X, nor could this be separated by ammonia; sulphur from a thiosulphate did not carry down any radioactinium from a preparation which was five months old. The rate of growth of radium was constant within the limits of experimental error for 500 days, from which we may conclude that the period of decay of the new substance is at least of the order of magnitude of radium

[1] Nature, **76**, 126. See also Phil. Mag., **14**, 733.
[2] See Hahn: Nature, **73**, 559 (1906).
[3] Nature, Sept. 26th, 1907. Also Am. J. Sci., **24**, 370.

D (12 years),[1] and its rate of growth from uranium (*i. e.*, from UrX) correspondingly slow.

Ionium, as Boltwood has named it, from the *ions* it produces, is chemically analogous to thorium and is precipitated along with it by oxalic acid, redissolving in ammonium oxalate, while actinium more nearly resembles lanthanum.[2] No method of separation from thorium has yet been given. It is characterized by α-rays of unusually short range, about 2.8 cm. in air;[3] its β-radiation is also more easily absorbed than that from uranium, the aluminium coefficient being 1.8. Agreeing with this, its activity is only about 0.7 to 0.8 of that of the equilibrium amount of radium. It gives no emanation.

A confirmation of all these properties is given in a note by Marckwald and Keetman.[4] Their method of extraction from pitchblende or autunite was to dissolve the ore in nitric acid, to convert into sulphates, filtering off those of lead, barium and radium, and to add hydrofluoric acid, which gave a very active precipitate, consisting chiefly of cerium, yttrium and thorium fluorides. These were dissolved by digesting with sulphuric acid and the thorium precipitated by oxalic acid. Ammonium carbonate, like the oxalate, redissolves ionium along with thorium, from which it follows that pitchblende residues must be relatively free from ionium, which is to be looked for in the uranium mother liquors.

Working from an entirely different standpoint, Hahn[5] has reached the same conclusion. In examining thorium preparations for the intermediate decomposition products, mesothorium[6] and radiothorium,[7] he found that commercial "pure" thorium salts contain considerable amounts of radium, though made from monazite which contains very little uranium. The amount of radium was greater the older the specimen, samples from 1 to 7 years old containing from 0.5 to 4×10^{-9} gram per 100 grams thorium. Direct experiment proved that the amount in a freshly prepared specimen of thorium nitrate was doubled in 2 months. When the thorium was precipitated as oxalate, the radium in the filtrate showed no increase in 4 months, in which time also 1 mg. of radiothorium, with an activity of about 100,000, prepared by precipitating barium sulphate in a solution of thorianite, showed no increase in

[1] Meyer and Schweidler: Physik. Z., **8**, 457 (1907).
[2] Giesel: Ber. d. chem. Ges., **40**, 3012.
[3] Nature, Oct. 10th, 1907. Am. J. Sci., **25**, 289.
[4] Ber. d. chem. Ges., **41**, 49 (1908).
[5] *Ibid.*, **40**, 4415.
[6] *Ibid.*, **40**, 1462 and 3304.
[7] P. Roy. Soc., **76**, 115 (1905). Jahrbuch d. Radioact., **3**, 330.

its small radium content. The radium parent, which is quite distinct from and independent of thorium, is thus seen to be concentrated in the process of manufacture of thorium salts (a trade secret). Assuming that none is lost and that the sand contains 0.3 per cent uranium to 5 per cent ThO, Hahn calculates that the observed growth of radium would maintain in equilibrium the amount which should theoretically accompany the uranium of the ore, if the decay period is 2600 to 3200 years.

The existence of ionium, the parent of radium, may therefore be considered as proved. A paper by Boltwood on his discovery is announced for the May number of the *American Journal of Science.*

B. B. TURNER.

THE ATOMIC WEIGHT OF TELLURIUM.

In a recent number of the *Berichte*,[1] W. Marckwald points out that the question of the exact atomic weight of tellurium has been under constant discussion and investigation since the Mendeléeff-Meyer arrangement of the elements in the Periodic System was first suggested, for in the case of this element the position assigned to it from a study of its chemical properties is not in agreement with the rule that the elements are arranged in the order of increasing atomic weights, as tellurium, with a higher atomic weight than iodine, precedes the latter.

The author has made a series of determinations of the atomic weight of this element with very carefully purified material and believes he has been able to prove that the true atomic weight is less than that of iodine and therefore in agreement with the theory.

He calls attention to a complete summary of all the work on this question recently prepared by A. Gutbier,[2] and discusses the more important methods that have been used for determining the atomic weight of tellurium.

(*a*) The conversion of the metal into the oxide by the action of nitric acid. Brauner[3] ascribes the unsatisfactory results with this method to the fact that some of the oxides of nitrogen are retained until the temperature is reached at which the oxide begins to volatilize.

(*b*) By determining the bromine in the tetrabromide by titration, Brauner obtained concordant results, which were confirmed by Chikasige,[4] with an average value of 127.71.

[1] Ber. d. chem. Ges., **40**, 4730 (1907).
[2] Sitzungsber. d. physik.-medizin. Soz. in Erlangen, **37**, 270 (1905).
[3] Monatsh. Chem., **10**, 411 (1898).
[4] J. Chem. Soc., **69**, 881.

(*c*) A number of investigators have used the method which depends upon the transformation of the dioxide into the metal. Staudenmaier,[1] using altogether, in two determinations, 3.5 grams, by reduction with hydrogen obtained an average of 127.57, which was also very closely approximated by Pellini. Heberlein obtained by this method the value 126.99 and Gutbier five results varying from 127.55 to 127.68. The latter investigator obtained almost the same results when the reduction took place in the wet way, using hydrazine as the reducing agent. Unfortunately, in no case where the dry method was used was the water, formed in the reduction, weighed.

(*d*) The basic nitrate method, depending upon the conversion of the compound $(TeO_2)_2HNO_3$ into the dioxide by heat. This method, first suggested by Norris, Fay and Edgerly,[2] may be open to the same criticism as the first method, the possibility that oxides of nitrogen are retained.

By this method, in a long series of experiments, Koethner obtained concordant results, recently confirmed by Norris, varying from 127.55 to 127.66. Gutbier obtained values varying from 125.8 to 127.8. One very strong objection to the use of this method is the great sensitiveness of the basic nitrate to moisture, which makes it necessary to remove the mother liquor with absolute alcohol.

(*e*) Telluric acid has also been used as the starting point in the determination of the atomic weights. Staudenmaier transformed the hydrate into the oxide and obtained an average result of 127.16. By reduction to the metal he obtained 127.28. Gutbier, using the same methods, but weighing the water formed, got 127.65 and 127.34. Heberlein found 126.72.

All experiments to show that the value as found was incorrect, owing to the presence of small amounts of a substance with a higher atomic weight, have failed.

The author separated 1500 grams of carefully purified telluric acid by several hundred crystallizations into twenty fractions and found no difference between the first and last fractions. Norris, Fay and Edgerly had carried out similar experiments with the compound K_2TeBr_6 with negative results. Having obtained the very pure telluric acid, the author determined the atomic weight of tellurium, using every precaution which was suggested by the results of the previous investigators. The material was first dried to constant weight in a vacuum

[1] Z. anorg. Chem., **10**, 189.
[2] This Journal, **23**, 105.

desiccator over sulphuric acid. When this substance was heated the following reaction took place:

$$H_6TeO_6 = TeO_2 + O + 3H_2O.$$

Instead of heating this material in a glass flask, as the previous investigators had done, the author used a platinum vessel and avoided errors in weighing by using as a counterpoise another vessel similar in every way. The vessel was heated by an electric stove, which heated only the bottom and thus allowed the upper part to remain cool and so condense any vapors of the oxide that might be formed. The temperature was raised very gradually, to prevent caking, until it reached 650° C. In some cases, in order to displace the oxygen from the vessel and to determine whether any of the material was lost as a volatile substance, a special cover was used which was so constructed that a current of dry air could be passed through the flask while the material was being heated. No evidence of loss was found.

In one case, No. 4, in the following table, the lower result is due to a very rapid heating, as the author conducted the experiment rapidly to determine when the decomposition was complete. The fractions used for the determinations were the first, ninth and twentieth. No. 4 was not included in the results:

No.	Fraction.	Weights of H_6TeO_6.	Weights of TeO_2.	Loss of weight (per cent).	Te.	Deviation from mean.
1	IX.	8.6277	5.9884	30.591	126.93	+0.08
2	I.	12.2680	8.5135	30.604	126.84	±0.01
3	I.	13.0051	9.0244	30.609	126.80	—0.05
4	XX.	8.6415	5.9947	30.629	126.65	.....
5	XX.	8.4588	5.8696	30.6095	126.80	—0.05
6	XX.	8.0113	5.5599	30.591	126.94	+0.09
		50.3699	34.9558	30.602	126.85	

The experiments led to the unexpected result that the atomic weight of tellurium is Te = 126.85 ±0.02 (probable error), a value lower than iodine (126.97) and 0.75 unit less than the value considered most reliable by the International Commission. The author says it is very improbable that this method could introduce such an error and points out that not only do some of the earlier determinations approach very close to his, but that the determination of the carbon in diphenyl telluride, made by Steiner, give a value below 127, varying between 126.1 and 126.7. Brauner, as well as Gooch and

Peters, in a careful study of the composition of tellurium dioxide, point out that the results are always too high and the latter workers state that the results obtained would agree with the theoretical if tellurium had an atomic weight of 127 instead of 127.5. The author refers to the very disagreeable physiological results of working with these compounds.

J. E. G.

REVIEWS.

ANNUAL REPORTS OF THE PROGRESS OF CHEMISTRY FOR 1906. Issued by the Chemical Society. Vol. III. London: Gurney & Jackson. 1907.

This valuable publication of the London Chemical Society is made up of the sections below named: General and Physical Chemistry, by Alexander Findlay; Inorganic Chemistry, by P. Phillips Bedson; Organic Chemistry—Aliphatic Division, by H. J. H. Fenton; Organic Chemistry—Homocyclic Division, by Julius B. Cohen; Organic Chemistry—Heterocyclic Division, by John Theodore Hewitt; Stereochemistry, by William Jackson Pope; Analytical Chemistry, by Alfred Chaston Chapman; Physiological Chemistry, by W. D. Halliburton; Agricultural Chemistry and Vegetable Physiology, by John Augustus Voeleker; Mineralogical Chemistry, by Arthur Hutchinson; Radioactivity, by Frederick Soddy.

Each section is, in fact, a carefully prepared report presenting the results of investigations that appear to the author to be the most important of the year. It is therefore something like R. Meyer's Jahrbuch der Chemie, from which it differs in this respect, that it does not contain references to as many original articles while, in general, giving more space to the most important ones.

The object the writers have in view is thus stated by W. D. Halliburton, who prepared the report on Physiological Chemistry. He says: "I imagine further that it is not the object of such a report as this to epitomise still further the epitomes which have monthly made up the bulk of the Journal, but rather to give the writer * * an opportunity to enlarge upon certain aspects of the science with which he happens to be more familiar, and to exercise that right of comment which is denied to him when he merely presents an abstract."

A statement by Frederick Soddy, who prepared the report on Radioactivity, will be of general interest. It is this: "It may be stated without fear of contradiction that the theory that the atom is made up entirely or to any substantial extent

of electrons is now generally regarded as being very much open to question. From spectroscopic and other evidence it is certain that electrons are universal constituents of atoms, but for the further very sweeping deduction that the atoms are composed of electrons there never has been much positive evidence in the past, while against the view some definite experimental evidence can now be urged."

POST'S CHEMISCH-TECHNISCHE ANALYSE. Handbuch der analytischen Untersuchungen zur Beaufsichtigung chemischer Betriebe, für Handel und Unterricht. Dritte, veremhrte und verbesserte Auflage. Herausgegeben von PROFESSOR DR. BERNHARD NEUMANN. Erster Band, Drittes Heft. Braunschweig: Friedrich Vieweg u. Sohn. 1907. pp. 488–814. M. 7.

This section includes three chapters, those upon Iron, Nonferrous Metals and Salts of the Metals Other than the Alkalies and Alkaline Earths. The first is written by Professor A. Ledebur. This is in itself a guarantee that the results of long experience are incorporated in its pages and the methods selected are doubtless those which he has found reliable. The methods chosen represent essentially European practice and the American reader will again have occasion to wonder why it is that German authors so persistently avoid all reference to such convenient and useful procedures as the volumetric determination for phosphorus, in which the reduction of the molybdenum, by passing the solution through a column of powdered zinc, is substituted for the tedious solution of the zinc and the assumed reduction of the oxide MoO_3 to $Mo_{12}O_{19}$. The entire omission of any description of the determination of carbon by combustion in oxygen is also noteworthy, since this must still be regarded as a technical procedure which serves as a court of appeal when the results by other methods are questioned.

The subdivisions of the chapters are: Ores, Fluxes, Cast and Wrought Iron, Slags.

The second and third chapters are written by Professor B. Neumann, and include the analysis of sixteen of the more common metals, as well as tungsten, uranium, vanadium and molybdenum. The salts of ten of the common metals are discussed in the last chapter. The methods are selected from a wide range of authors and publications, and seem to indicate a thorough knowledge and good judgment in the choice of procedures. The high standard of the work, as a whole, is maintained in the section under review.

H. P. TALBOT.

POST'S CHEMISCH-TECHNISCHE ANALYSE: Handbuch der analytischen Untersuchungen zur Beaufsichtigung chemischer Betriebe, für Handel und Unterricht. Dritte, vermehrte und verbesserte Auflage. Herausgegeben von DR. BERNHARD NEUMANN. Zweiter Band, Zweites Heft. §§ 22–27. Braunschweig: Friedrich Vieweg und Sohn. 1907. Price, M. 10.

The fact that Section 22 (144 pp.) on the analytical methods used in the beet-sugar industry is an abridgment by Dr. Frühling of the sixth edition of his well-known work and that Section 26, on distilling (66 pp.), is largely taken by Dr. Hanow from the eighth edition of Märcker-Delbrück, bespeaks their excellence. Section 23 (72 pp.) on starch, dextrin and grape sugar is contributed by Dr. Parow, of the "Institut für Gärungsgewerbe und Stärkefabrikation." Section 24, on brewing (46 pp.), is by Drs. Vogel and Bleisch. Dr. Kulisch writes Section 25 on wine (90 pp.), and Dr. Rothenbach, also of the "Institut für Gärungsgewerbe," is responsible for Section 27, on vinegar, acetic acid and its compounds, and wood spirit (32 pp.).

The volume is characteristically German in that it ignores mention of all authorities not German and is consistently a compendium of German methods. Perhaps, when the index appears, in the due course of completion of the work, some references may be found to the classic method of the great English brewing chemists, Brown and Morris, for instance, or to some French analyst. The reviewer has failed to find but one reference to the work of a foreigner, and that on some trivial point of detail, among the host of authorities which are given.

The work is also characteristically German in the thoroughness of its editing and the excellence of its illustrations and typography.

GEO. W. ROLFE.

ELECTRO-ANALYSIS. By EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Fourth edition, revised and enlarged, with forty-two illustrations. Philadelphia: P. Blakiston's Son & Co. 1907. pp. 336. Price, $2.50 net.

The demand for this well-known and admirable laboratory guide, in this comparatively new field of quantitative analysis, is shown by the rapidity with which the first three editions were disposed of. In the preface to this, the fourth edition, the author states that "It appeared advisable to omit from this edition the several sections relating to the various sources of the current, particularly those in which the older forms of battery were described. * * *

The greater portion of the new material presented in the pages which follow refers to the rapid precipitation and sepa-

ration of metals, the use of a mercury cathode with rotating anode, and the employment of a new cell in the determination of cations and anions."

The rapid growth of electro-analysis in the last decade or two is really due to the application of physical-chemical principles to the subject of quantitative analysis, and it would certainly make any analyst think, to hear the leading authority in this field in this country state, as he does in his preface, "that the estimation, for example, of barium and chlorine, in barium chloride, may be made in an hour or less."

It is not too much to say that the subject of analytical chemistry has, through electro-analysis, been fundamentally changed, if not, in part, actually revolutionized. We owe many of our best methods in this field to the author of this book.

The work of the printer also is admirably done, the book being well adapted in every respect to use in the laboratory. It will find, for a long time to come, a growing demand.

H. C. J.

IMMUNO-CHEMISTRY. The Application of the Principles of Physical Chemistry to the Study of the Biological Antibodies. By SVANTE ARRHENIUS. New York: The Macmillan Co. 1907. $1.60.

"Considering the very brief period during which physical-chemical methods have found application to the study of biological problems, the advance which has been made is very remarkable and there is every reason to believe that in the future, as the methods become more and more extensively applied, the advance will become more rapid and widespread."

These words of Al. Findlay could not have found a better verification than is afforded by this new book on immuno-chemistry by one of our greatest physical chemists.

The war between the two views concerning the nature of immuno-reactions has raged now for several years. Under such circumstances it seems of the greatest importance that the new ideas which Arrhenius has brought into this question are clearly set forth, not so much to convince the opponents as to allow the impartial reader to judge by himself as well as to interest new workers in this promising field.

It may be well to recall that for years Ehrlich has led the way in the study of the intricate questions concerning the toxins and antitoxins. To explain these phenomena he has built up a system almost as complicated as the structural formulae of organic chemistry. However, when Ehrlich

tried to decide the question whether we are dealing here with chemical reactions or which physiological phenomena in the body, his "side chains" failed to give an answer and, moreover, failed to point to a method of experimental attack. Arrhenius, unencumbered by such hypotheses, has taken up this problem from the point of view of chemical equilibrium of incomplete reactions, to which the law of mass action must apply. To the physical chemist, who reads through the overwhelming mass of experimental evidence collected in this book, there can be no doubt that Arrhenius has attacked the problem in a way which from our present state of knowledge seems the best, if not the only one. Hence, as long as his opponents have not obtained quantitative results which contradict those of Arrhenius and his school, we may safely entrust ourselves to his guidance.

Since the book is of interest to medical men primarily, the special chapters are preceded by a geneal discussion of the reversibility of reactions, of velocity of reaction in homogeneous and heterogeneous systems, and of equilibria of absorption processes. One chapter each is devoted to the neutralization of diphtheria toxin, ricin, saponin and snake-venom, to the compound haemolysins and to the precipitins and their antibodies. The literature bearing on any of these questions has been considered most completely.

Although this new book is the outcome of a series of lectures delivered to the students at Berkeley, California, it makes considerable demand on the reader. This may be due to the fact that the subject is as yet quite unwieldly. At times, however, when the reasoning becomes quite involved and hard to follow, one feels the need of an Ostwald to make the difficult subject-matter more intelligible. Still a careful study of the book cannot be recommended too highly to every one interested in this question and to those who intend to keep pace with the rapid progress being made in the applications of physical chemistry to various phenomena.

GEORGE W. HEIMROD.

VORTRÄGE FÜR AERZTE ÜBER PHYSIKALISCHE CHEMIE. Von DR. ERNST COHEN. Zweite, vermehrte und verbesserte Auflage, mit 53 Figuren im Text. Leipzig: Verlag von Wilhelm Engelmann. 1907. pp. 264. M. 8; bound, M. 9.

The appearance of this book has already been referred to in THIS JOURNAL.[1] The early appearance of the second edition shows that it has met a want among physicians, who are now called upon, so frequently, to apply the fundamental

[1] THIS JOURNAL, **30**, 165.

principles of Physical Chemistry. It is fortunate that they have been supplied with a work from such a reliable and authoritative source, and equally fortunate that they have realized their opportunity and have used the book. H. C. J.